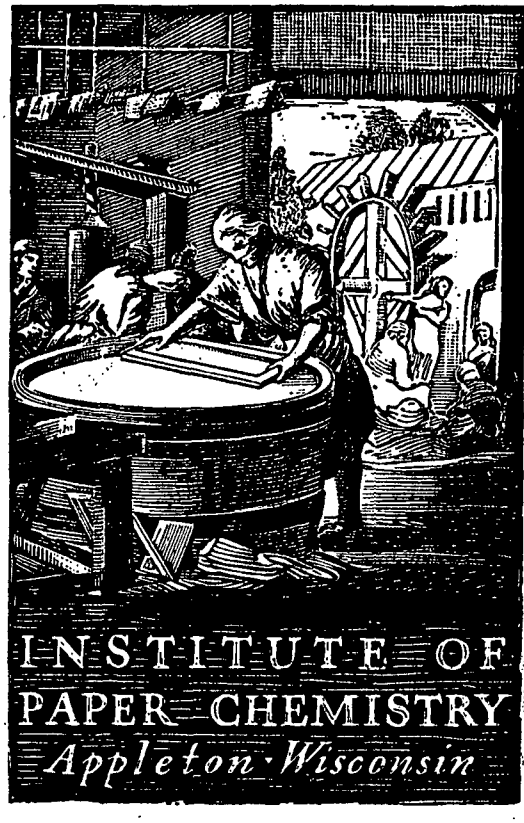

AUTOMATIC INSTRUMENTATION FOR CHEMICAL ANALYSIS OF PULP

Project 2634

Report One

A Progress Report

to

MEMBERS OF GROUP PROJECT 2634

June 14, 1967

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

AUTOMATIC INSTRUMENTATION FOR CHEMICAL ANALYSIS OF PULP

SUMMARY

Following a literature survey, selected methods of measuring residual lignin in pulp were briefly examined in the laboratory to study their reliability and to determine their adaptability to automation. These initial feasibility studies showed: (1) the impracticality of attempting direct automation of titrimetric methods involving the use of potassium permanganate, (2) that spectrophotometric and colorimetric methods for measuring lignin in liquor as an inverse function of lignin in pulp should be investigated more deeply, and (3) that reaction of pulp with nitric acid holds possibilities of being developed into a simple and general colorimetric procedure for measuring lignin in pulp.

Following the initial studies, an intensive investigation of several lignin in liquor methods led to the conclusion that this approach to measuring degree of delignification of pulp had no general, reliable or precise application. Statistical analysis of the data revealed a high degree of inverse correlation between lignin in liquor and lignin in pulp, but also showed that a relatively small variation in any of many cooking conditions, in addition to wood species variations, contributed to a considerable imprecision in the results. The mean relative error of estimating lignin in pulp from lignin in liquor measurements was found to be $\pm$ 12% of the "true" value. This approach was abandoned.

The initial studies indicated that a little-used colorimetric method of measuring lignin in pulp by reaction with nitric acid produced results directly related to Klason lignin and to Kappa numbers. A broad study of this

method was undertaken, using both commercial pulp samples and pulp produced in laboratory cooks, and covering a yield range from 45 to 70%. Within this range, it was found that the nitric acid method was directly related to both Klason lignin and Kappa number with a precision of about ± 2% for laboratory pulps and about ± 4% for commercial pulps.

In the laboratory cooks a variety of softwood species was used and one hardwood, aspen, was used. The same conversion factor for calculating Kappa numbers from the nitric acid method results applied to all softwoods, but a different factor was found for aspen. A third factor was found for all of the commercial pulps.

The essential simplicity of the nitric acid method makes it the most suitable method available for adaptation to an automated procedure. This adaptation is currently under way, together with the initial stages of development of automatic sampling, and these two activities will form the major portion of the next phase of work.

INTRODUCTION

As a result of Proposal 1056, Project 2634 was established in August, 1966. At present the group membership stands at 22 companies.

The proposal was originally divided into three separate but interrelated objectives:

1. The development of an automatic means of obtaining a known sample of fiber from a pulp slurry.

2. The development of an automatic method of measuring pulp "hardness" or degree of delignification.

3. The development of an automated procedure for measurement of specific sugars in pulp hydrolyzates as a means of determining carbohydrate content of pulp.

When the project was established it was amended by eliminating the third objective, largely at the request of the participating companies.

The basic principle of the sampling system is outlined in the proposal. The practical design, however, is expected to depend to a major extent on the automatic analytical procedure chosen for determining pulp "hardness." It was therefore decided to study first the various procedures for determining lignin, based on their accuracy and their ease of automation.

Lignin is not a completely defined substance, i.e., its chemical formula and its molecular weight are not established, although much is known about its structural components. At the present time, lignin is regarded as an indefinite polymer of substituted phenylpropane groupings with the major functional units being hydroxyl, methoxyl, and phenyl rings.

No entirely satisfactory procedure exists for quantitative determination of lignin, i.e., a method giving the absolute amount of lignin in all cases. The basic problem is one of dealing with a complex biochemical, high-polymer, colloidal system which does not respond to gradual, "harmless" chemical treatment, whereas drastic methods quickly cause changes in such a polymeric, easily condensable substance. There exist, however, a number of proposed methods. Since no method is absolutely quantitative, the merits of each method should be evaluated in connection with its particular use. The method to be chosen should also be evaluated according to the type of information desired.

Since the aim of this project is to develop an automatic method for determining pulp "hardness," further discussion will be limited to chemical and physical methods with potentialities for direct or indirect determination of residual lignin in pulp.

ULTRAVIOLET SPECTROPHOTOMETRY

Ultraviolet spectrophotometry has been extensively employed in the study of the chemistry and molecular structure of lignins (1-3). The direct absorption spectra of lignins and lignosulfonic acids in solution show two maxima, a strong one at 200-205 nm. and a weaker one at 280 nm. The maximum near 280 nm. has been frequently cited as supporting evidence of guaiacyl, syringyl, and related structures. The absorption at these maxima has been used by several authors (1, 4-9) as quantitative methods for determining lignin content in digester liquors. As pointed out several times (4-9), the absorption at 280 nm. is strongly influenced by the presence of carbohydrate degradation products, while the absorption at 205 nm. is influenced by the inorganic chemicals used in the kraft and sulfite processes. Some success has been

achieved in monitoring digester liquors for lignin by measuring the absorption at either of these wavelengths. However, a study of the work of these authors (4-9) shows that each of them used a different approach to circumvent the difficulties involved, and that none of these approaches have resulted in a method applicable to any situation except the particular one investigated.

Recently, the absorption obtained from the difference in absorptivities of the ionized (alkaline solution) and nonionized (neutral or acid solution) forms of lignin has been used in studies of the molecular structure of lignin (10-15). Such difference spectra display a strong peak at about 250 nm. and a weaker peak at about 300 nm. Minima are found near 229 and 278 nm. In Fig. 1 is shown a typical difference spectrogram of kraft lignin. It is supposed that these maxima are characteristic for the absorption of the phenolate ion of simple substituted aromatic hydroxyl compounds (10-13). Phenolic compounds in which the hydroxyl group is conjugated through the ring with a carbonyl group have maxima near 250 and 350-400 nm. (10-13). Thus, while the 250-nm. maximum is common to both types of compounds, the 300-nm. maximum of the difference spectrum is characteristic for hydroxyl groups without such conjugation. Both of these wavelengths have been utilized for determining phenolic hydroxyl group content in lignin preparations (14, 15).

A procedure (16) based on difference absorption at 250 nm. has been described for determining lignins and lignosulfonic acids in polluted water, but, as far as is known, has never been applied to measuring lignin in digester liquor. Johnson, et al. (17) have found that lignin in wood can be measured at 280 nm. after dissolution of the finely ground sample in acetyl bromide–acetic acid solution. They found, however, that pulp was not readily dissolved. Sjöström and Enström (18) dissolved wood and pulp in Cadoxene and measured the

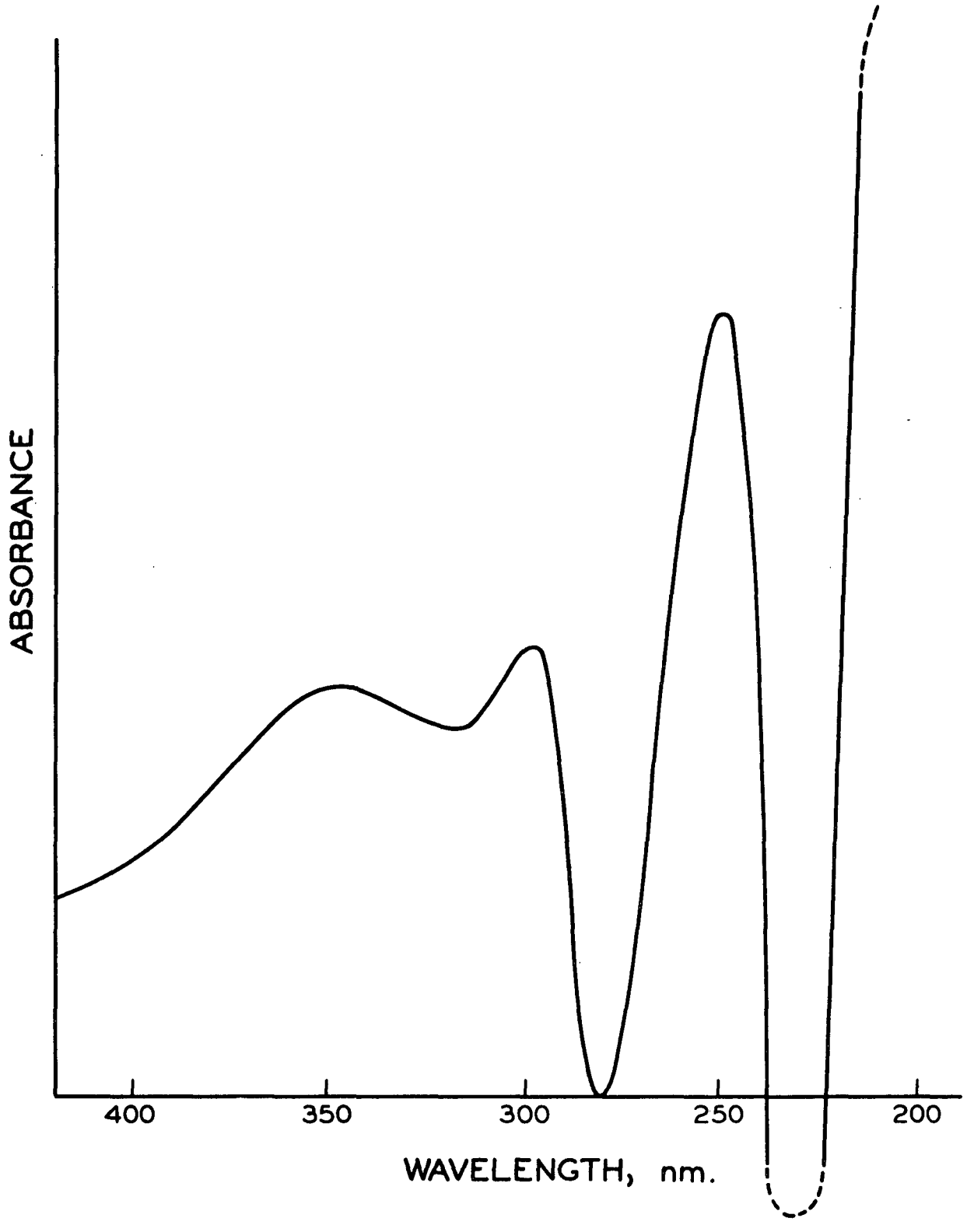

Figure 1. Difference Spectrum of Kraft Black Liquor

absorption of lignin at 280 nm. Pulp with a Kappa number below 20 could be analyzed by this procedure. Nakajima and Hachihama (19) found that Brauns native lignin in wood and pulp reacts quantitatively with aqueous o-phenol-sulfonic acid to form a water-soluble product measurable by U.V.-spectrophotometry.

COLORIMETRY

There are several more or less specific color reactions between organic and inorganic chemicals and lignin. Among these, is the well-known Pearl-Benson reaction, devised in 1940 by Pearl and Benson (20), which in various modifications (21-23) has come into wide use for determining spent liquor in water. It is based upon a supposed reaction of lignin with nitrous acid to form nitroso derivatives which, in alkaline solution, tautomerize to more highly colored quinone oxime derivatives (23). It appears that this reaction involves the phenolic groups in lignin and is thus based on reaction of the same groups measured in the difference spectrum method described above.

Bartunek (24) extracted a yellow color from pulp upon heating it with dilute nitric acid and measured the color at 420 nm. Although he applied this only to high purity pulps containing very small amounts of lignin, there appears to be no reason why it could not be applied to unbleached or higher yield pulps.

OXIDIMETRIC METHODS

The main method in this category involves the use of acid permanganate solution. Assuming that permanganate reacts with lignin only, leaving carbohydrates unchanged, this method consists basically of oxidizing a known and fixed amount of pulp with a standard solution of acid permanganate for a fixed time and at a fixed temperature. The amount of permanganate used is a measure

of the lignin content of the pulp. Several modifications exist, the permanganate number and the Kappa number being the best known. Both are standardized TAPPI procedures. The permanganate number (25) of a pulp is defined as "the number of milliliters of 0.1N $KMnO_4$ solution absorbed by 1 gram of moisture-free pulp under conditions specified and carefully controlled." The Kappa number (26) is defined as "the number of milliliters of 0.1N $KMnO_4$ consumed per gram of moisture-free pulp under conditions specified in the standard procedure. The results are corrected to be equivalent to a 50% consumption of the permanganate in contact with the specimen." Other, and similar, tests for lignin in pulp are the "chlorine number" (27), and a direct test for hypochlorite bleach requirement (28).

GRAVIMETRIC METHOD

The most widely used method based on this principle is the well-known Klason lignin procedure, which consists of hydrolyzing the cellulose with strong mineral acid, followed by gravimetric determination of the undissolved lignin. Several modifications of this method exist, but the procedure standardized by TAPPI (31) is the one most widely used, and the one regarded as a reference method. The method itself is tedious, and about two days are usually required to obtain the results. Consequently, it is not well suited to routine control purposes.

DISCUSSION

This condensed review shows that lignin, whether in solution or in the original solid phase, is presently measured by applying one of two general methods: (1) Ultraviolet spectrophotometry or colorimetry applied to the wholly or partially solubilized sample. (2) Direct measurement in the solid phase by oxidimetric titration or gravimetric analysis.

The only one of these procedures obviously not suitable for adaptation to completely automated methods is the direct solid phase analysis by gravimetric methods. The essential problem, then, was to examine the many modifications of the remaining procedures to see which, if any, offers good possibilities for automation. Of these, the preferred choice would be simply to automate the Kappa or permanganate method, if the main consideration was to obtain a test of the digestion product. If, on the other hand, it appeared more desirable to obtain a measure of delignification during digestion, then it again seems obvious to attempt to apply a colorimetric or spectrophotometric method to the liquid phase and obtain an inverse measure of the lignin left in the pulp.

Considering other methods, those which are based on dissolving the pulp sample were rejected because they would require a water-free pulp sample, which the proposed sampling system would not be able to deliver. The only other method which looked fairly attractive was Bartunek's nitric acid method (24) because it involved a single inexpensive reagent and analytical operations which would be fairly simple to automate. It was therefore decided to investigate this method in some detail, along with other initial investigations of the possibility of automating the "K" number procedure, and of measuring dissolved lignin in digester liquor by spectrophotometric and colorimetric means.

INITIAL EXPERIMENTS

Because of its wide use in the pulping industry, the permanganate number method was chosen as an initial object of experimentation to determine its adaptability to automation. In addition, Bartunek's nitric acid procedure appeared so essentially simple, that it, too, was selected for initial investigation. Among those methods applicable to digester liquor, the method of ultraviolet differential spectrophotometry appeared to offer a major inherent advantage over the more common methods of direct measurement at 205 and 280 nm., respectively: the possibility of eliminating the effect of substances other than lignin that also absorb U.V. light. Finally, although it has apparently never been applied to digester liquor, there appeared to be no reason why the Pearl-Benson method could not be used, especially since it seemed quite suited for automation.

PERMANGANATE METHOD

Since this test is performed directly upon the pulp, the major problem after quantitation of the sample is to choose an instrumental system capable of handling the fiber slurry according to the dictates of the procedure. Previous experience with the AutoAnalyzer and its use in the permanganate oxidation of water samples (30) indicated it could be used with liquid samples containing small amounts of particulate matter. Consideration of other instrumental systems commercially available showed that there was really none suitable to the purpose.

Experimentation showed that a stable dynamic system for the permanganate method could be attained with the AutoAnalyzer where the sample contained no particulate matter, and, further, that this instrument could,

under certain conditions, handle aqueous suspensions of fibers without clogging the internal system. However, it was difficult to obtain an even distribution of fibers in the liquid flow pattern of the AutoAnalyzer. As a consequence of this effect, the reduction of the permanganate color varied quite a lot within the samples and resulted in uneven records and in a poor reproducibility. Further experimentation showed that it is not possible to maintain in the AutoAnalyzer system the strict conditions required for the permanganate procedures. The AutoAnalyzer is a dynamic system which creates several problems in the handling of suspensions. A more advantageous approach would apparently be to base an automatic system on a discontinuous operation, i.e., to simulate the manual operations by automatic means. Principally, this could be achieved by some type of automatic titrator. Such a solution, however, is not attractive because of the maintenance problems usually involved in such complicated mechanical and electronic systems. Also, this would involve the design of a new instrument. Such an instrument also would require a sampling system designed to deliver a chosen amount of fiber reproducibly. The sampling system to be investigated in this project will probably be based on delivering a sample of known but slightly variable amount of fiber. Because of the strict requirements of the permanganate procedures, it was concluded that automating this method is impractical.

DIFFERENCE ULTRAVIOLET SPECTROPHOTOMETRY

Manual experiments with a Beckman DU spectrophotometer were made using a commercial kraft lignin (Indulin A) as a standard, and kraft black liquor samples obtained from laboratory cooks of southern pine. These cooks were identical, except for the cooking time, and resulted in black liquors with lignin contents over a wide range. A series of standards was made to cover an equal concentration range.

Standards and samples were diluted to appropriate concentrations for reading on the spectrophotometer, and each was divided into two portions. One portion of each was adjusted to pH 6.8 with a phosphate buffer, and the other portion was adjusted to pH 12.1. The absorbance of each standard and each sample at the two different pH values was read at 250 nm. and at 300 nm., and the differences between the absorbances at the two pH values at these two wavelengths were obtained. Readings were made against the appropriate buffer in distilled water. A white liquor sample was treated similarly.

It was found that, for Indulin A, a plot of concentration vs. the difference in the absorbance at the two pH values gave a straight line at both wavelengths, and that, using this plot as a reference curve for the black liquor samples, a good approximation of their known lignin contents was obtained.

In Table I are given examples of readings obtained from samples measured at 300 nm. It is noted that the difference absorbance (Δ) of the white liquor at 300 nm. is small in spite of the fact that its concentration is about 10 times higher than those of the black liquor samples. The corresponding difference absorbance reading at 250 nm. was 0.70. It is also seen from Table I that the difference readings of glucose, furfural, and hydroxymethylfurfural are negligible at 300 nm. The concentrations of these substances are much higher than those expected to be present in digester liquors. Both aldehydes give rise to an absorption reading at both pH values. They are, however, the same in both cases, so that the difference technique eliminates interference from these types of compounds.

TABLE I

ABSORBANCE READINGS AT 300 nm.

		Kraft Liquor		White Liquor	Glucose	Furfural	Hydroxymethyl-furfural
Dilution →		1:1000	1:2000	1:100	1 g./liter	2.5 mg./liter	1 mg./liter
Absorbance	pH 12	0.630	0.312	0.026	- 0.003	0.069	0.021
	pH 6.8	0.394	0.192	0.097	- 0.008	0.066	0.018
	Δ	0.236	0.120	-0.071	0.005	0.003	0.003

These experiments indicated that difference measurements at 300 nm. are worthy of more extensive study as a means of determining lignin in spent liquors, and that white liquor constituents and carbohydrate degradation products formed during the cook would not interfere in the determination. An automated procedure was therefore devised for further experiments, using a Beckman DB spectrophotometer modified for use with the AutoAnalyzer.

The modifications in this instrument consist of a set of rectangular flow cells (6-mm. light path) and a converting unit for use with a Technicon recorder. The Beckman DB can be used for single-beam and double-beam difference operation, and both for scanning and for single wavelength operation.

The flow scheme shown in Fig. 2 was set up on the AutoAnalyzer, and an attempt was made to use it for difference absorption measurement at 300 nm. It was not possible, however, to obtain a noiseless recorded curve. A condition for differential measurement with a continuous system like the AutoAnalyzer is that the two samples must reach their respective flow cells exactly in phase. A very good phasing was achieved, but still the noise level was too high. The noise was found to be caused by improper design of the flow cells. Their internal

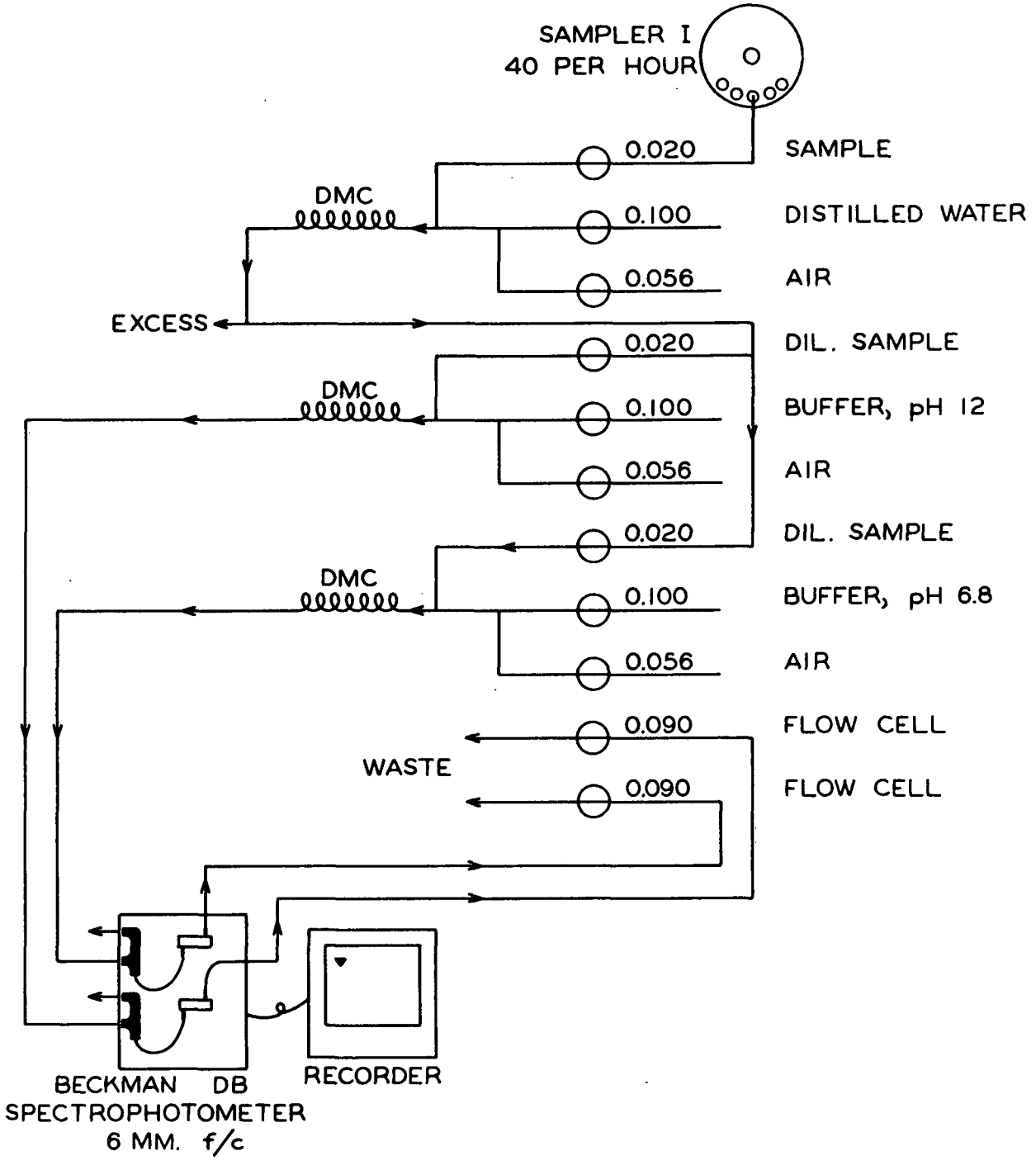

Figure 2. Flow Scheme for Automated Measurement of U.V. Absorbance of Black Liquors

volumes were too large, thereby causing a holdup in the liquid stream which resulted in an unphased turbulence in the cells. The flow scheme was, however, suitable for recording spectra of samples. This was done by shutting off the liquid flow when the samples had reached their respective flow cells. The spectra were then recorded from 420-210 nm. One problem arose during experimentation with this method. The spectrum of a sample which had not been exposed to air before analysis showed lower absorptivities than that which had been exposed to air. Furthermore, the absorptivities of the unexposed samples showed at some wavelength ranges lower absorptivities than the difference spectrum of distilled water. This indicated that the effect of some interfering compounds was eliminated by contact with air. No such effect was observed with Indulin A. Some experiments bringing the samples into increasing contact with oxygen were therefore performed. The spectrophotometer was set up for single-beam operation and a sample was analyzed both at pH 12 and 6.8, and it was brought into increasing contact with oxygen before the buffer was added. It was found that at pH 12 the absorbance was not influenced by increasing oxygen contact. At pH 6.8, however, a decreasing absorbance was observed by increasing oxygen contact. Consequently, the difference absorbance increased with increasing oxygen contact. A small glass coil filled with ceramic spheres was then placed in the sample line and operated with oxygen flow concurrent with the sample flow to provide an oxidized black liquor sample.

This manifold was used for recording difference spectra, and also for absorbance measurements at fixed wavelengths, in which latter case the Beckman DB was switched to single-beam operation. Then the reference cell channel of the manifold was disconnected and the reference cell was filled with distilled water. Buffered sample was pumped through the measuring cell.

Two absorbance values were obtained on each sample: at pH 12 and at pH 6.8. These were subtracted to give the difference values. Occasionally, in later work, direct measurements were made at 280 nm. also, in which case the sample was not buffered, and the buffer solution was replaced by distilled water.

AUTOMATED PEARL-BENSON METHOD

Upon obtaining a satisfactory automated procedure for obtaining reproducible, noise-free recordings of U.V. absorbance of black liquor samples, attention was turned to the development of a similar method using the Pearl-Benson technique.

Several slightly different manual procedures for this technique are described in the literature. The procedure given by Goldschmid and Maranville (22) was chosen as a basis for adaptation to the AutoAnalyzer. Their procedure is as follows: To a 150-ml. sample add 3 ml. of 10% sodium nitrite and 3 ml. of 10% acetic acid; mix thoroughly and let stand for 15 minutes. Add 6 ml. of 2N ammonium hydroxide and mix again. The reacted sample is measured at 430 nm. in a suitable colorimeter against a blank prepared from the same sample in a similar manner except that the sodium nitrite solution is omitted. This is necessary to compensate for background color in the sample.

The flow scheme of the Pearl-Benson method finally adapted for the AutoAnalyzer is shown in Fig. 3. Two pumps, a double-coil heating bath, a dual-beam phototube colorimeter, and a two-pen recorder are used. The sample is aspirated from the sampler, segmented with air, diluted with distilled water (1:14.5), and mixed. A small part of the diluted sample is divided into two equal parts and each part is reintroduced in the system, one to the sample line

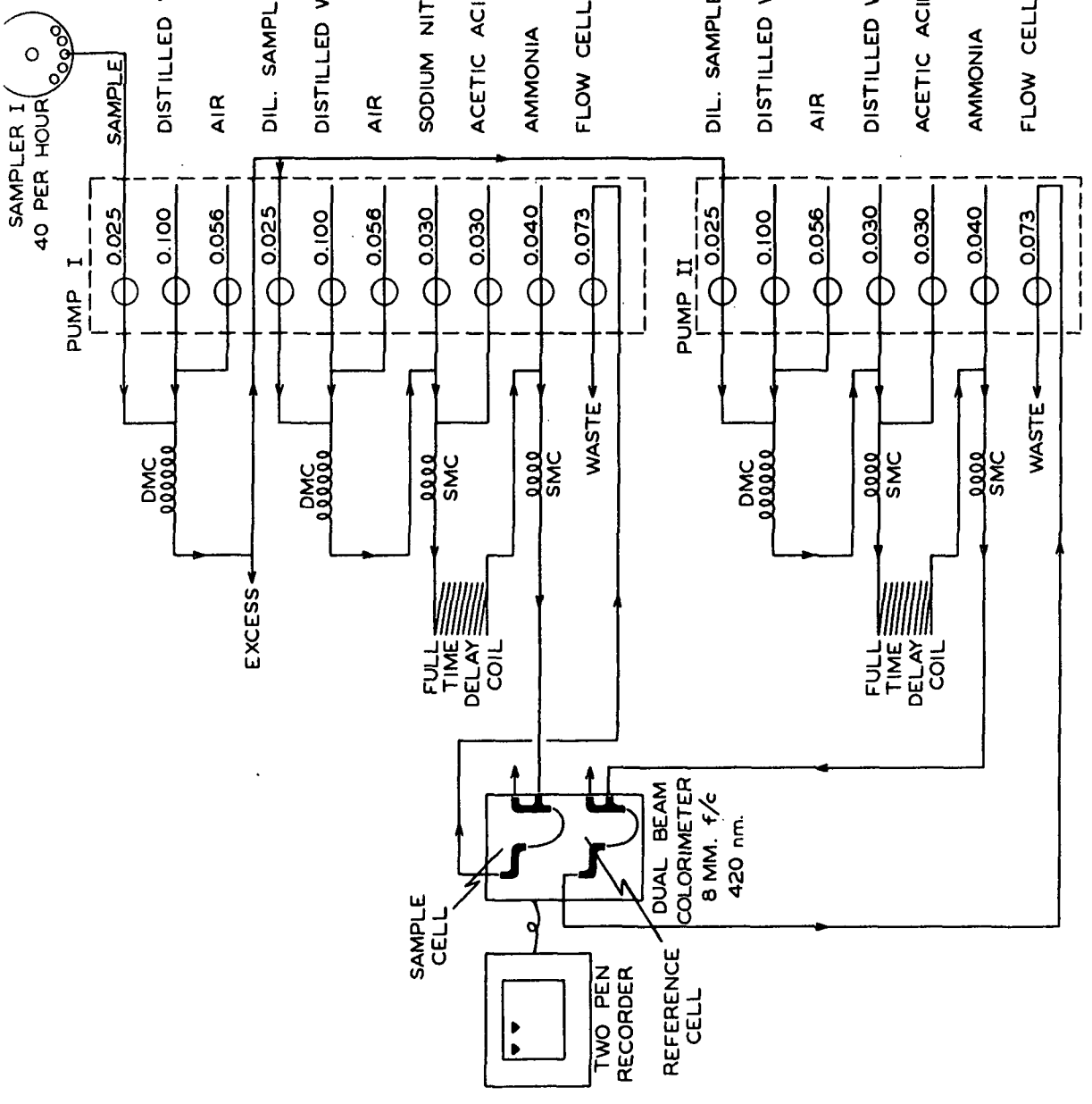

Figure 3. Flow Scheme for Automated Pearl-Benson Method

(upper part of flow diagram) and the other to the reference line (lower part of flow diagram). The sample is again diluted with distilled water (1:14.5), segmented with air, mixed, and sodium nitrite and acetic acid are added. After mixing, the stream is pumped through one coil in a double-coil constant-temperature bath (20°C.) to allow for color development. After emerging from the bath, the sample is made alkaline with ammonia, mixed, and pumped through the colorimeter where the color is measured at 420 nm. The reference part of the sample is treated in a similar manner except that an equal amount of distilled water is added instead of sodium nitrite.

Each sample gives two peaks on the recorder, one by the reacted part of the sample and one by the unreacted part. Their absorbance values are read, and the difference between the two gives the net absorbance due to "lignin" in the sample.

The automatic sampler was set at a speed of 40 samples per hour, but the samples were placed only in every second hole in the sampler plate in order to obtain sufficient "washout" between samples.

SIMULTANEOUS U.V.:PEARL-BENSON METHOD

Since it was desired to compare the UV-spectrophotometric and Pearl-Benson colorimetric methods for determining lignin, it was considered convenient to combine those methods into a simultaneous system by eliminating the reference lines in the flow diagrams shown in Fig. 2 and 3. The combined flow diagram is shown in Fig. 4. The system consists of a sampler, two pumps, a constant-temperature bath, a single-beam colorimeter, a Beckman DB spectrophotometer (single-beam operation), and a two-pen recorder. The sample is aspirated from the sampler, segmented with air, diluted with distilled water

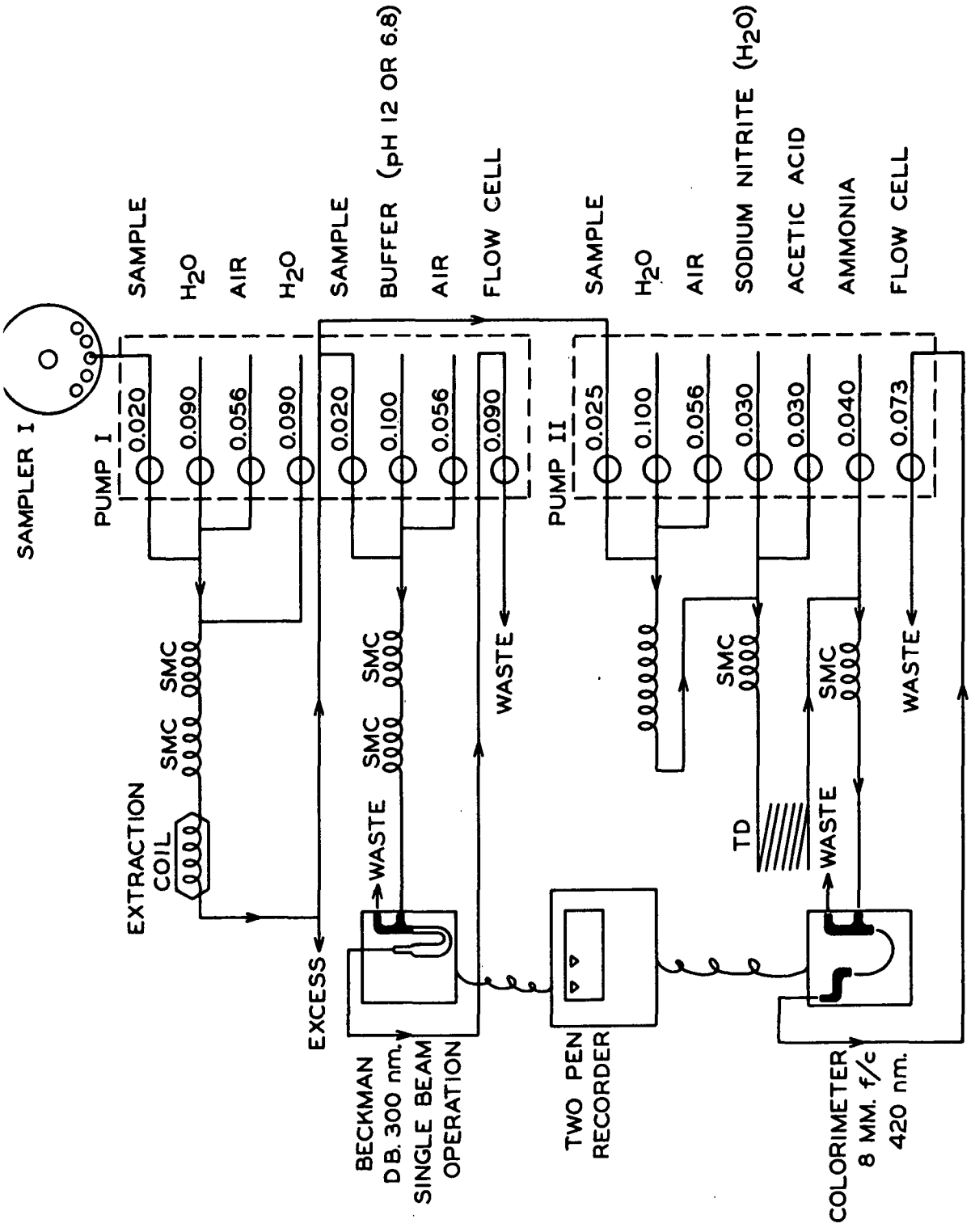

Figure 4. Flow Scheme for Simultaneous U.V. Pearl-Benson Method

(1:14.5), and mixed. A small part of the diluted sample is divided into two equal parts and each part is reintroduced, one to the U.V. line and the other to the colorimetric line. The U.V. sample is mixed with buffer of pH 12, segmented with air, and pumped through the sample cell of the Beckman DB. (The reference cell is filled with distilled water.) The absorbance is measured at 300 nm. The colorimetric sample is mixed with water, segmented with air, and sodium nitrite and acetic acid are added. After mixing, the stream is pumped through the constant-temperature bath (20°C.). After emerging from the bath, the sample is made alkaline with ammonia, and the color is measured at 420 nm. in the colorimeter.

In order to obtain the U.V. absorbance at pH 6.8, and to correct the Pearl-Benson measurements for absorbance due to the original color of the sample, the samples are sent through a second time, pumping buffer of pH 6.8 and substituting distilled water for the sodium nitrite. The reagents used in this simultaneous method are listed in Table II. A commercial lignosulfonate, Toranil, and a kraft lignin, Indulin A, were both used as "standards." Indulin A was dissolved in dilute sodium hydroxide and Toranil in water.

Figures 5 and 6 show, respectively, the calibration curves obtained by using Indulin and Toranil as "standards" with both methods.

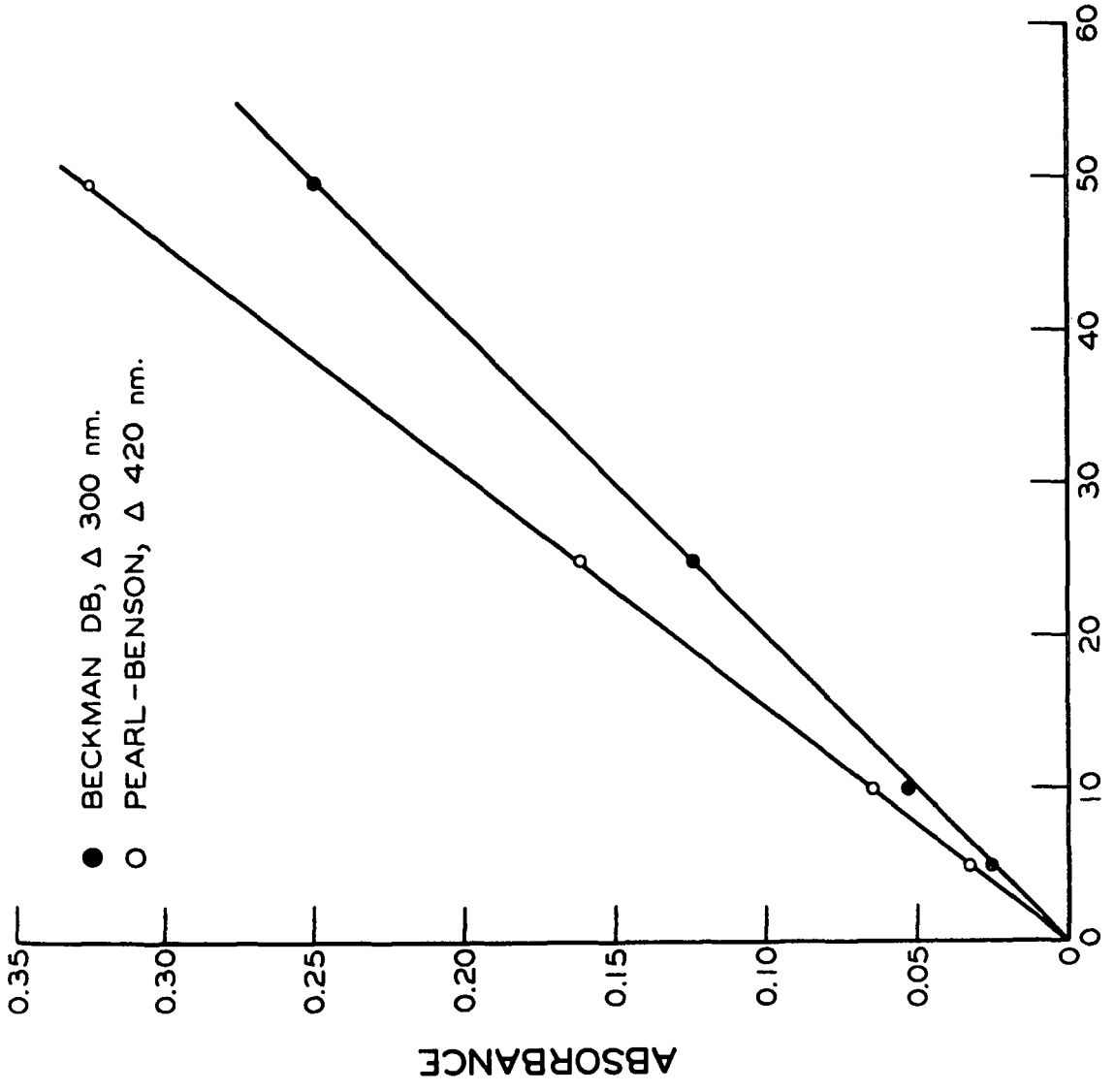

Figure 5. Calibration Curves of Indulin (Kraft Lignin) by Simultaneous U.V.:Pearl-Benson Method

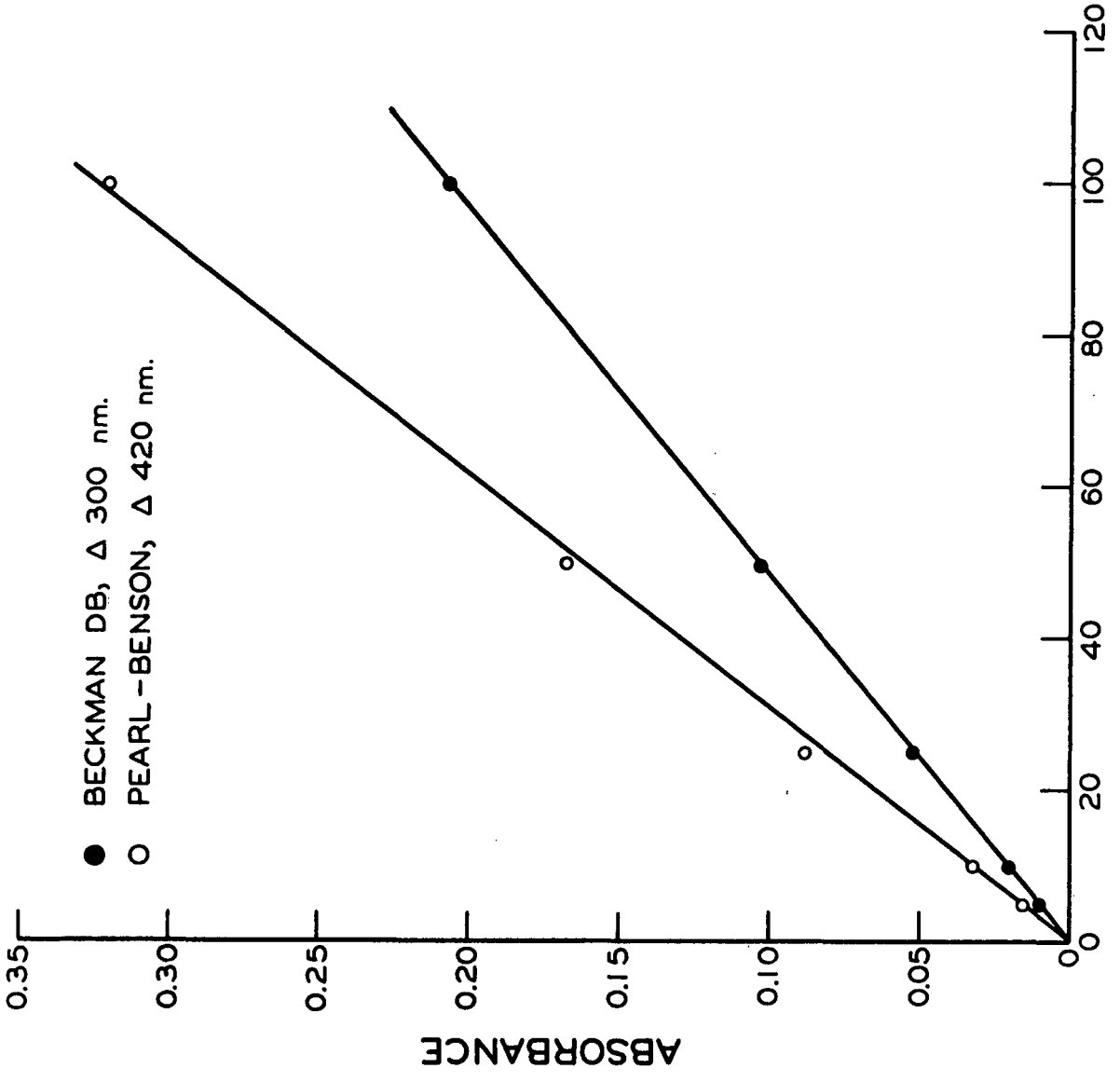

Figure 6. Calibration Curves of Toranil (Sulfite Lignin) by Simultaneous U.V.: Pearl-Benson Method

TABLE II

REAGENTS FOR SIMULTANEOUS U.V.:PEARL-BENSON METHOD

U.V.-Spectrometric Method

Buffer of pH 12: Dissolve 13.7 g. of $Na_3PO_4 \cdot 12\ H_2O$ in distilled water and dilute to 1 liter.

Buffer of pH 6.8: Dissolve 18 g. $Na_2HPO_4 \cdot 12\ H_2O$ and 6.8 g. KH_2PO_4 in distilled water and dilute to 1 liter.

Pearl-Benson Method

Sodium Nitrite: Dissolve 5 g. $NaNO_2$ in 100 ml. of distilled water.

Acetic Acid: Dilute 1 part of glacial acetic acid with 9 parts of water.

Ammonium Hydroxide: Dilute 1 part of concd. ammonia with 9 parts of water.

There was available a series of black liquor samples from experimental kraft cooks made in 1964, and these were used for initial feasibility studies because most of the cooking data was at hand. The samples had been stored undisturbed in completely filled and sealed polyethylene bottles. These cooks were made in a multiunit microdigester system designed to permit the study of various pulping conditions as functions of pulping time. In addition, most of the yield and Klason lignin data were available for these cooks.

Table III lists the known cooking conditions for the four series of liquor samples used. Table IV lists for all of the samples the light absorbance readings obtained by the simultaneous U.V.:Pearl-Benson procedure. Table V shows two sets of lignin concentration values for all of the liquor samples.

One set is calculated by using Indulin A (kraft lignin) as a standard, and the other set is based on Toranil (sulfite lignin) as a standard.

TABLE III

COOKING DATA FOR OLD LIQUOR SAMPLES

I. Code: 6/4. Date: Sept. 19, 1964.

60 g./liter A.A., 40% sulf., temp. 140°C.

6:1 liq.-wood ratio. Charge: 20 g., o.d.

Cooking times, min.: 5, 15, 35, 75, 130, 190, 320.

II. Code: 9-1. Date: Sept. 10, 1964.

60 g./liter A.A., 40% sulf., temp. 160°C.

10:1 liq.-wood ratio. Charge: 20 g., o.d.

Cooking times, min.: 10, 15, 25, 40, 75.

III. Code: 9-2. Date: Sept. 10, 1964.

60 g./liter A.A., 40% sulf., temp. 160°C.

6:1 liq.-wood ratio. Charge: 20 g., o.d.

Cooking times, min.: 10, 35, 55, 55x.

IV. Code: 8-10. Date: Sept. (?), 1964.

Data unknown.

Cooking times, min.: 5, 15, 25, 45.

TABLE IV

LIGHT ABSORBANCE READINGS OF BLACK LIQUOR SAMPLES

Sample	Cooking Time, min.	U.V. at 300 nm. pH 12	pH 6.8	Δ	Pearl-Benson Sample	Blank	Δ
9-2	10	0.1272	0.0873	0.0399	0.0698	0.0271	0.0427
	35	0.3700	0.2373	0.1327	0.2247	0.0561	0.1686
	55	0.5673	0.3610	0.2063	0.3370	0.0717	0.2653
	55x	0.5351	0.3342	0.2009	0.3310	0.0647	0.2663
8-10	5	0.0186	0.0140	0.0046	0.0111	0.0022	0.0089
	15	0.2810	0.1795	0.1015	0.1725	0.0536	0.1189
	25	0.4485	0.2721	0.1764	0.2816	0.0816	0.2000
	45	0.6145	0.3956	0.2189	0.3946	0.1176	0.2770
9-1	10	0.0706	0.0414	0.0292	0.0340	0.0132	0.0208
	15	0.1135	0.0713	0.0422	0.0630	0.0200	0.0430
	25	0.1367	0.0870	0.0497	0.0996	0.0200	0.0796
	40	0.3098	0.1970	0.1128	0.1838	0.0410	0.1428
	75	0.4763	0.3044	0.1719	0.2818	0.0580	0.2238
6-4	5	0.0410	0.0177	0.0233	0.0132	0.0022	0.0110
	15	0.0969	0.0655	0.0314	0.0706	0.0177	0.0530
	35	0.2182	0.1367	0.0815	0.1307	0.0292	0.1015
	75	0.2708	0.1612	0.1096	0.1824	0.0410	0.1414
	130	0.4300	0.2654	0.1646	0.2716	0.0482	0.2234
	190	0.4685	0.2735	0.1950	0.3054	0.0580	0.2474
	320	0.5302	0.3078	0.2224	0.3635	0.0680	0.2955

The data in Table V show that there is close agreement between the U.V. method and the Pearl-Benson method when the results are calculated against Indulin A as a standard. When calculated against Toranil, however, the agreement between the two procedures is not as close, a result that is not surprising, since the samples are kraft liquor, and Toranil is lignosulfonate from the sulfite processes.

TABLE V

CALCULATED LIGNIN CONTENT OF OLD LIQUOR SAMPLES

Sample	Time, min.	G./Liter Against Indulin A		G./Liter Against Toranil	
		Δ U.V. (300 nm.)	Pearl-Benson	Δ U.V. (300 nm.)	Pearl-Benson
9-2	10	8.0	6.6	19.5	13.0
	35	26.5	26.0	65	51.0
	55	41.0	40.8	101	80.5
	55x	40.0	41.0	98.5	81.0
8-10	5	0.9	1.3	4.3	2.7
	15	20.2	18.3	50.0	37
	25	35.1	30.8	86.5	60.5
	45	43.6	42.7	107.5	84.0
9-1	10	5.8	3.2	14.2	6.3
	15	8.4	6.6	20.7	13.0
	25	9.9	12.2	24.4	24.0
	40	22.4	22.0	55.0	43.3
	75	34.2	34.4	84.5	68.0
6-4	5	4.7	1.7	11.4	3.3
	15	6.3	8.1	15.4	16.0
	35	16.2	15.7	40.0	30.8
	75	21.8	21.8	54.0	43.0
	130	32.7	34.3	81.0	67.8
	190	38.8	38.1	96.0	75.0
	320	44.3	45.3	109.0	89.5
Mean values:		23.0	22.6	56.9	45.0

The difference in the mean values between the two methods using Indulin A as reference were tested for significance by the paired comparison technique (see Appendix for formulae). The t-value obtained, 0.97, indicated that the difference was not significant at the 99% significance level.

The sum, lignin in liquor + lignin in pulp, should equal the lignin in the original wood. Since for three of the four series of liquor samples used, the corresponding pulp yields and their Klason lignin contents were known, such a lignin balance was calculated. The lignin in the liquor

was calculated by using for each individual sample the numerical mean value of the U.V. and the Pearl-Benson results, both against Indulin A, shown in Table V. These data are shown in Table VI.

The correlation between lignin content in pulp and in liquor was evaluated statistically using the outline given by Ezekiel (31), the formulae for which are given in the Appendix. The correlation coefficient of -0.970 indicates an inverse linear relationship, as could be expected.

Using the outline shown in the Appendix, the regression coefficient was found to be -0.74 and the regression line, regarding lignin in liquor as the independent variable X, was calculated to be represented by Equation (1).

$$Y = 5.66 - 0.74\ X \qquad (1).$$

Using the values in Table VI, lignin-in-liquor (X) is plotted against lignin in pulp, and the calculated regression line is drawn through the data points, as shown in Fig. 7.

Using lignin in pulp (Y) as the independent variable, another regression line, represented by Equation (2), can be calculated.

$$X = 7.37 - 1.26\ Y \qquad (2).$$

According to statistical theory, the regression lines so calculated will be identical in the case of absolute correlation ($r = \pm 1$). In the case of no correlation, the two lines will be at right angles to each other ($r = 0$). Both regression lines are shown in Fig. 8, yielding an illustration of the close inverse correlation between the lignin in liquor and the lignin in pulp values.

TABLE VI

LIGNIN CONTENT OF PULP AND LIQUOR

Sample	Time, min.	Yield, %	Klason Lignin in Pulp, %	Lignin in Liquor, g./liter	Total Lignin in Liquor, g.	Total Klason Lignin in Pulp, g.	Sum of Lignin in Pulp and Liquor
9-1	10	84.5	30.16	4.5	0.90	5.12	6.02
	15	80.5	28.12	7.5	1.50	4.52	6.02
	25	73.1	24.54	11.0	2.20	3.59	5.79
	40	62.6	18.80	22.2	4.43	2.35	6.78
	75	49.7	7.85	34.3	6.86	0.78	7.54
9-2	10	84.5	28.63	7.3	0.88	4.85	5.73
	35	70.4	22.68	26.2	3.15	3.18	6.33
	55	59.8	15.98	40.9	4.93	1.90	6.83
	55x	60.7	15.55	40.5	4.87	1.89	6.76
6-4	5	97.2	28.44	6.3	0.76	5.55	6.31
	15	84.0	29.64	7.2	0.87	5.03	5.90
	35	77.5	27.77	16.0	1.93	4.33	6.26
	75	72.3	24.70	21.8	2.62	3.58	6.20
	130	66.7	21.99	33.5	4.04	2.94	6.98
	190	64.8	19.93	38.5	4.64	2.58	7.22
	320	57.3	14.26	44.8	5.40	1.64	7.04
				Mean values:	3.13	3.35	6.48

Lignin in wood = 6.15 g. per digester.

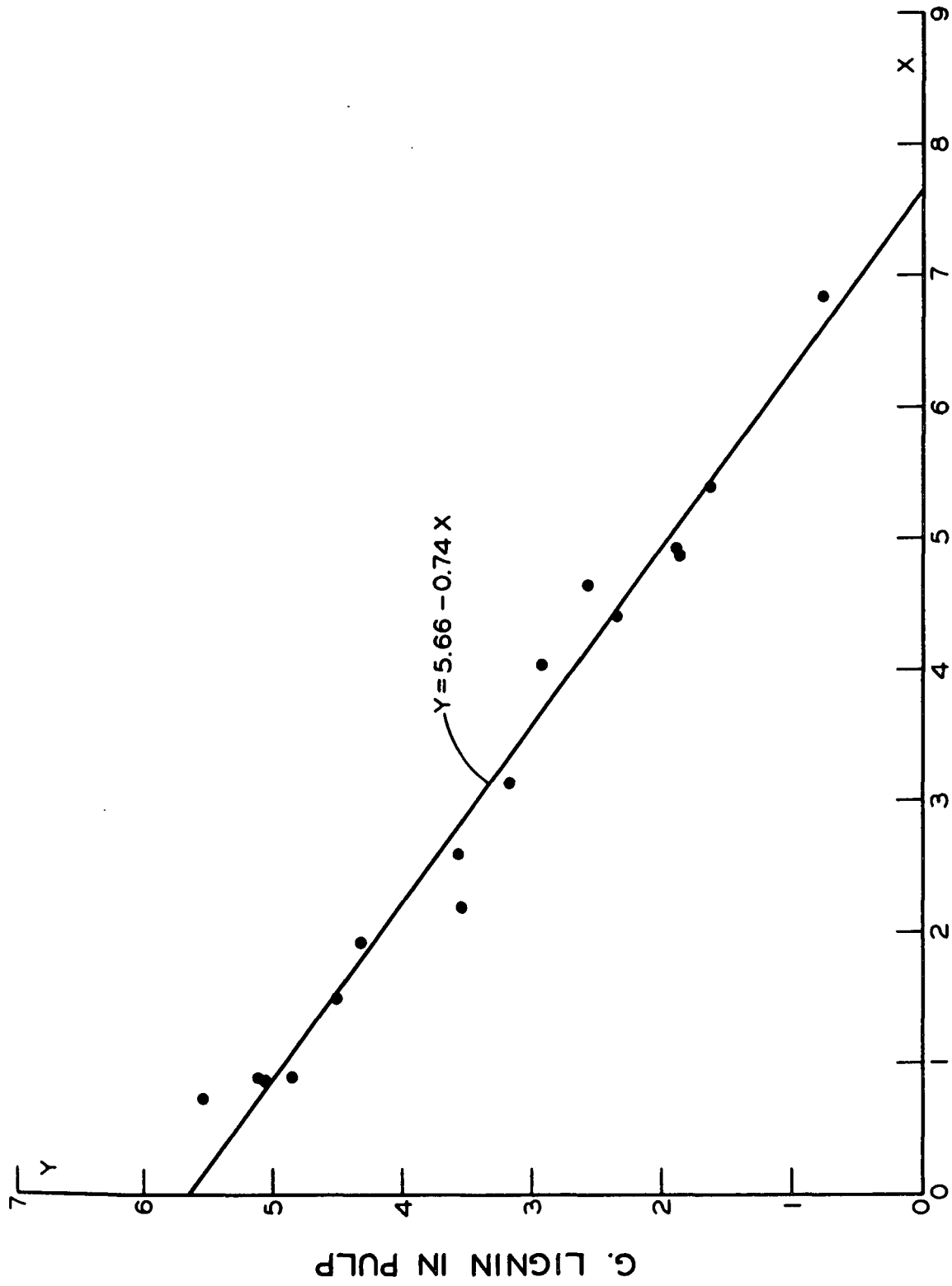

Figure 7. Relationship Between Lignin in Liquor and Lignin in Pulp

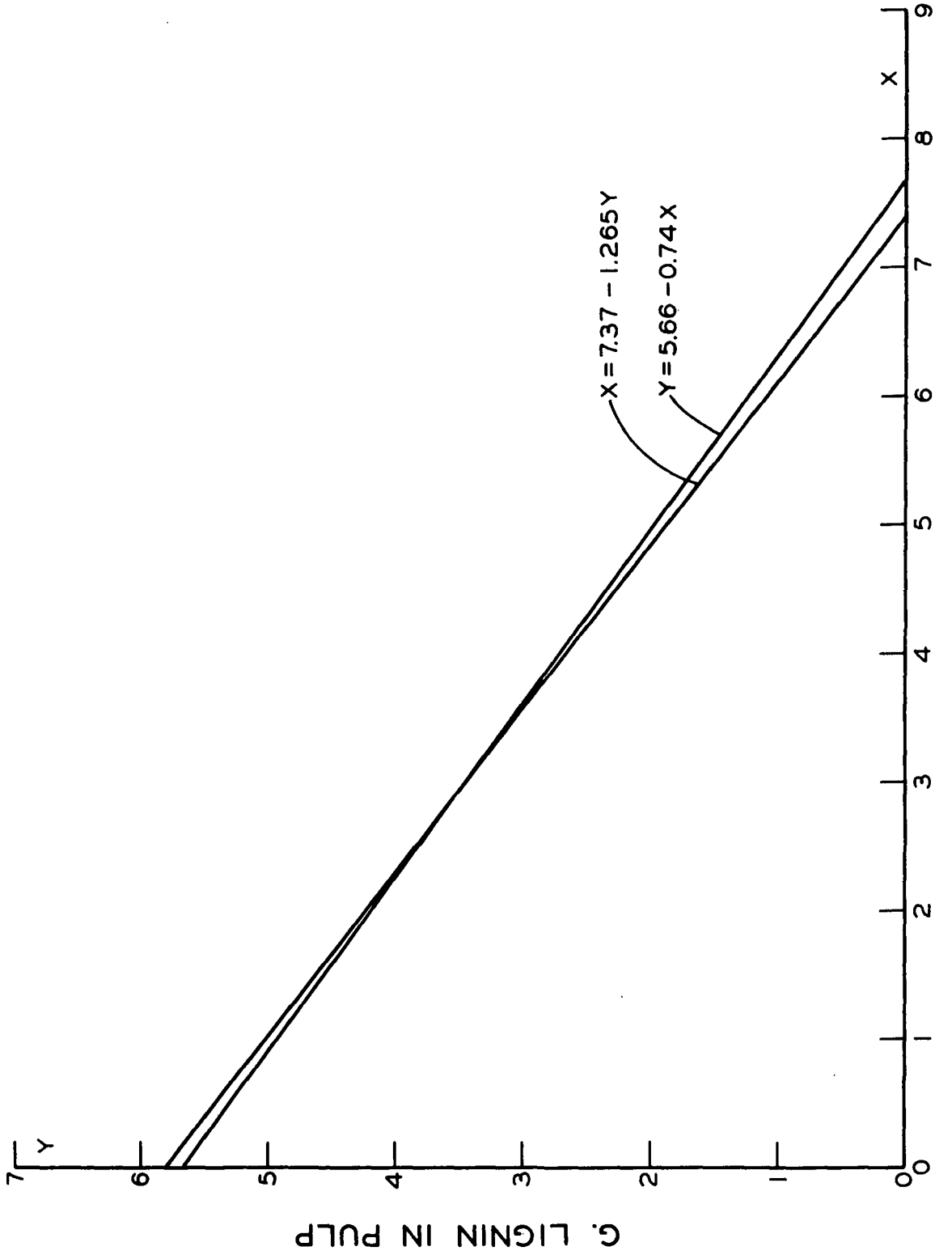

Figure 8. Regression Lines of Lignin in Pulp (X) vs. Lignin in Liquor (Y) Where Both Are Regarded as Independent Variables

The regression equation given in Equation (1) may be used to estimate the lignin content in the pulp when the lignin content in the liquor is known. In order to estimate the standard error of the whole regression line, the standard errors of the estimate, the regression coefficient, and the mean estimated values of $\underline{Y}$ must be known. These are obtained from Formulas (9), (13), and (15) in the Appendix. Their values were found to be: $\underline{\underline{S}}_{YX} = 0.36$, $\sigma_{b_{\underline{\underline{YX}}}} = 0.049$, $\sigma_{\underline{\overline{Y}}'} = 0.090$.

The standard error of the estimated value of lignin in pulp ($\underline{Y}'$) for selected values of lignin in liquor may then be calculated.

In Table VII are given the calculations and the calculated values of the standard error of $\underline{Y}'$.

TABLE VII

STANDARD ERROR OF ESTIMATED VALUE OF LIGNIN IN PULP

Selected Value of $\underline{x}$	Departure from Mean	$[\sigma_{b_{\underline{\underline{YX}}}} (\underline{x}-\underline{\overline{x}})]^2$	$\sigma_{\underline{\overline{Y}}'}^2$	$\sigma_{\underline{Y}'}^2$	$\sigma_{\underline{Y}'}$
0.13	-3.00	0.0216	0.0081	0.0297	0.172
1.13	-2.00	0.0096	0.0081	0.0177	0.133
2.13	-1.00	0.0024	0.0081	0.0105	0.102
3.13	0	0	0.0081	0.0081	0.090
4.13	1.00	0.0024	0.0081	0.0105	0.102
5.13	2.00	0.0096	0.0081	0.0177	0.133
6.13	3.00	0.0216	0.0081	0.0297	0.177
7.13	4.00	0.0385	0.0081	0.0466	0.216

In Fig. 9 are plotted 95% confidence limits of the estimate of $\underline{Y}$, thus giving the range within which the true regression line probably lies.

In order to use the regression equation given in Equation (1) for future individual predictions of the lignin content in pulp when the lignin content in the liquor is measured, the standard error of the predicted value is calculated from Equation (18) in the Appendix. The standard errors calculated are given in Table VIII, and in Fig. 10 are plotted the 95% confidence limits of a future estimate of $\underline{Y}$.

TABLE VIII

STANDARD ERROR OF PREDICTED VALUES OF LIGNIN IN PULP

Selected Values of $\underline{x}$	$\sigma \underline{Y}$
0.13	0.40
1.13	0.392
2.13	0.384
3.13	0.371
4.13	0.384
5.13	0.392
6.13	0.400
7.13	0.420

It can be seen that, on the basis of these initial investigations utilizing old cooking data, a broader study is warranted of the possibility of measuring residual lignin in pulp as an inverse function of the lignin dissolved in black liquor, and that the U.V. difference method and the Pearl-Benson colorimetric method are valuable tools in such a study.

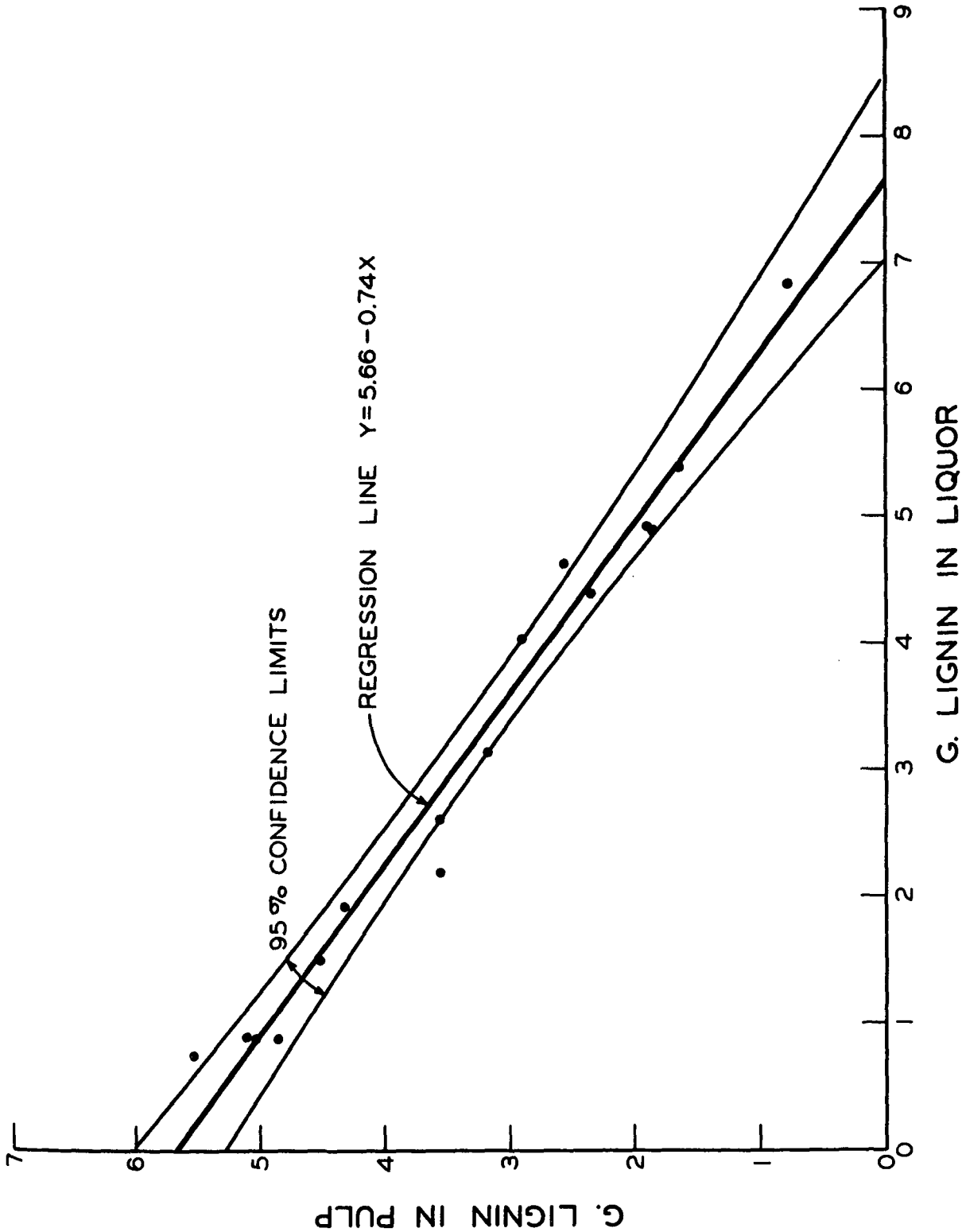

Figure 9. Experimental Regression Line for Lignin in Liquor vs. Lignin in Pulp with 95% Confidence Limits of the Location of the True Regression Line

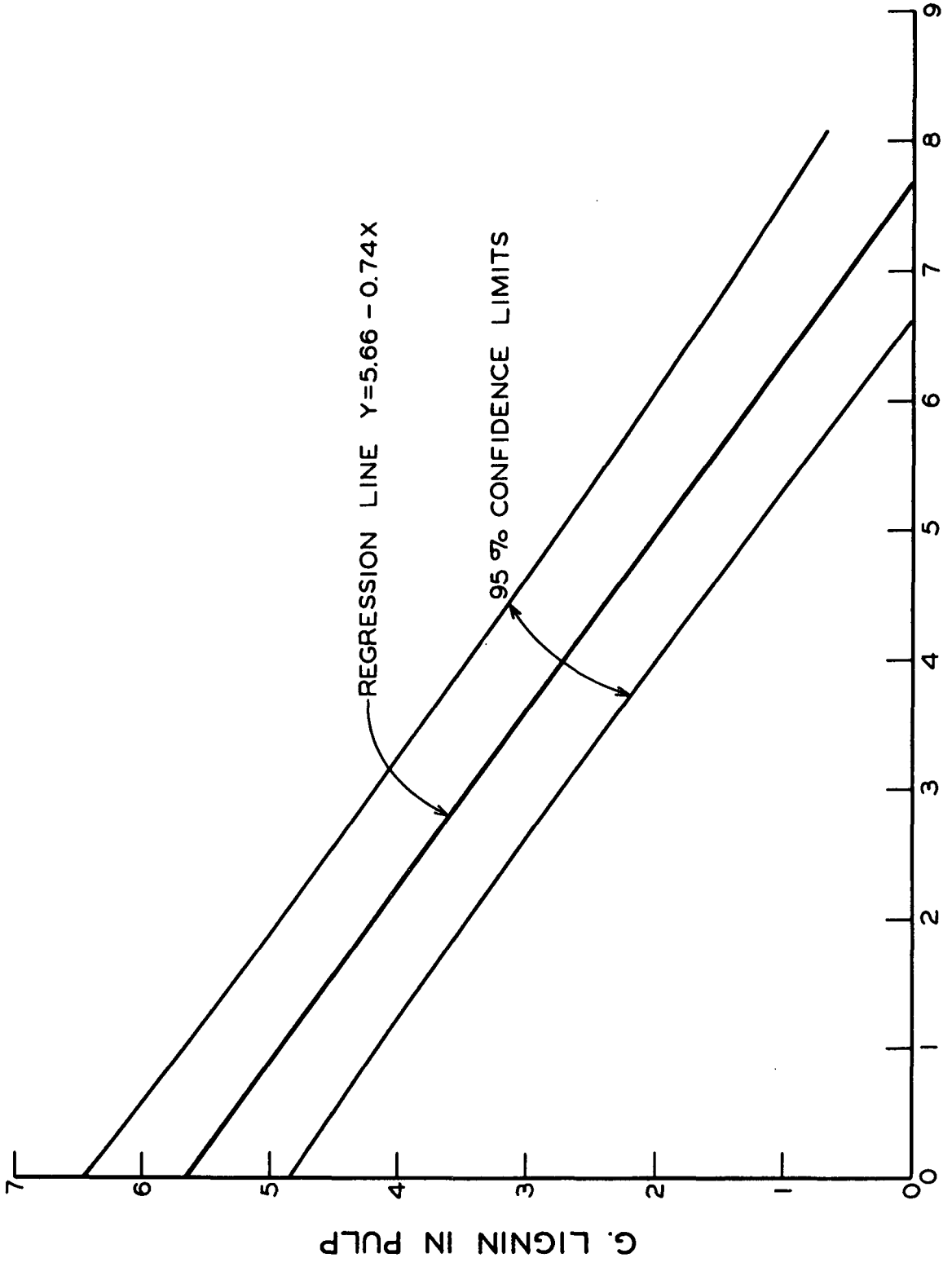

Figure 10. 95% Confidence Limits of Future Predictions of Lignin in Pulp Based on Present Measurement of Lignin in Liquor Values

NITRIC ACID METHOD

An extensive literature exists concerning the reaction of aqueous nitric acid with lignin. It is known that nitric acid "dissolves" most of the lignin in wood, without affecting the carbohydrates to any appreciable extent. There is still some confusion regarding the reactions involved, but there is evidence that nitro compounds are formed during the reaction. Electrophilic side-chain replacement by a nitro group has been shown to occur in the nitration of a number of guaiacyl derivatives in organic solvents (32, 33). Such a reaction product, 2,4-dinitro guaiacyl, has been isolated on nitrating sprucewood meal, and is apparently derived from free guaiacyl end groups in lignin (33). Oxidation reactions also take place to a large extent. Only simple degradation products have been identified so far: monomeric phenols and nitrophenols, oxalic, acetic, and formic acids, carbon monoxide, and carbon dioxide. Reported reduction products from nitric acid include nitrogen, nitrous oxide, nitric oxide, nitrogen dioxide, and hydrogen cyanide. Aromatic methyl ethers suffer partial demethylation, resulting in a loss of methoxyl content in the lignins.

Two essentially different methods for determining lignin in pulp with nitric acid have been described: Kürschner's (34) gravimetric method and a colorimetric procedure used by Seidel (35), Richter (36), and Bartunek (24). Kürschner treated the pulp with a mixture of ethanol and concentrated nitric acid and weighed the isolated "nitrolignin." He claimed results superior to the Klason lignin method.

During the reaction of dilute nitric acid with wood or pulp, a yellow-colored product is formed in solution. The first ones to utilize this were

Seidel (35) in 1907 and Richter (36) in 1912. Seidel attached most importance to the rather complicated analysis of the evolved gases, using the amounts of gases formed during the reaction as a measure of the lignin content. Richter based his procedure on the colorimetric measurement of the yellow color. A standard pulp was used as a reference. The next work published on this procedure appeared in 1959 by Bartunek (24). He applied a modification of Seidel's procedure to pulp with lignin contents below 1%. The working procedure of Bartunek is as follows: Fifteen grams of moisture-free pulp are cut into 5-mm. squares and placed in a glass-stoppered flask containing 100 ml. of 13% nitric acid at 40°C. After 45 min. at this temperature, the mixture is filtered through sintered-glass. The yellow filtrate is cooled rapidly and its intensity immediately measured in a colorimeter. A comparison standard is prepared by dissolving 0.100 g. of potassium dichromate in 1000 ml. of distilled water. Bartunek's procedure was used on spruce sulfate viscose pulps for more than 30 years, and an excellent correlation between lignin content and filterability of the pulp was reported. He investigated the yellow reaction products of a variety of pulps for their extinction curves in the range 200-400 nm., and found that the curves were quite similar, having a distinct maximum at 261 nm. and another, broader maximum at 330-338 nm. He showed that the maximum at 261 nm. was also obtained when benzene was treated with nitric acid. Phenol gave the same maxima as obtained for the pulps investigated, thus indicating that reaction of lignin with nitric acid involves the aromatic groups.

Because the essential simplicity of the colorimetric nitric acid method makes it highly adaptable to automation, some experiments were made which were designed to explore its applicability to high-lignin-content pulps. The procedure used was essentially similar to Bartunek's, but the pulp was ground to

pass through a 40-mesh screen before reaction with nitric acid. Color measurements were made with a Beckman DB recording spectrophotometer, using 10-mm. matched silica cells. It was found that, when 30 mg. of pulp were mixed with 50 ml. of 14% (V/V) nitric acid and heated at 70°C., maximum color intensity was obtained after about twenty minutes.

Figure 11 shows three spectra recorded from 330 to 500 nm.: one of the yellow extract from black spruce kraft pulp, one of the yellow extract from aspen kraft pulp, and one of the nitric acid itself. The spectra of the pulp extracts were made against the nitric acid as a blank, and the nitric acid spectrum was made against distilled water. It is seen that the yellow-colored reaction product formed by reacting pulp with nitric acid shows two distinct maxima, one at 425 nm. and another at 340 nm. The absorption of nitric acid is negligible from 500 to 350 nm., from where it increases sharply, having a strong absorption at 340 nm. Therefore, the latter maximum is not suitable for analytical purposes. The maximum at 425 nm., however, is well suited both from an analytical and a practical point of view, especially because any filter photometer may be used at this wavelength. Bartunek made no observations of the absorption at this particular wavelength, and neither did his results show any indication of a definite maximum in this range. It was decided to investigate the effect of the variables of the method on the absorption of the yellow color at this particular wavelength.

The procedure used is as follows: 30-mg. samples were weighed into 100-ml. beakers, 50 ml. of 14% (V/V) nitric acid were added to each, and the beakers with their contents were placed in a water bath. After heating for a fixed period of time at a fixed temperature, the contents of the beakers were filtered through Whatman no. 40 filter paper and the absorption was immediately measured at 425 nm.

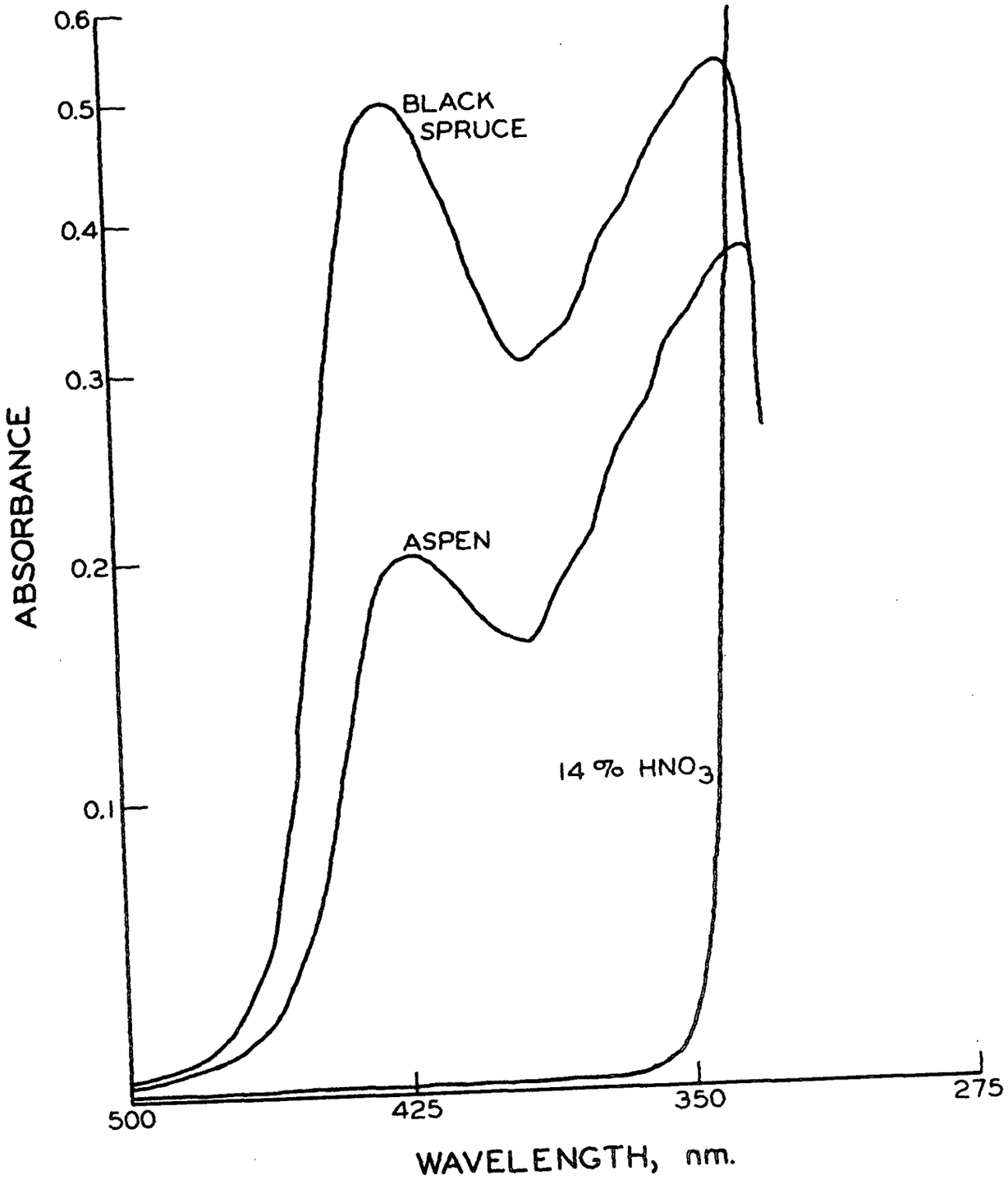

Figure 11. Absorbance Spectra of the Reaction Product with Nitric Acid of Black Spruce Kraft and Aspen Kraft Pulps Plus the Nitric Acid Itself

Bartunek used a solution of potassium dichromate as a reference standard. The absorption spectrum of this compound in distilled water is shown in Fig. 12. This spectrum shows a constant absorption in the range 420-440 nm., suggesting that potassium dichromate is a suitable reference "standard" for the nitric acid method. Solutions containing 50, 100, 200, and 400 mg. of $K_2Cr_2O_7$ per liter were prepared and their optical densities were read against distilled water as a blank at 425 nm. The calibration curve in Fig. 13 shows that Beer's law is obeyed.

These experiments show that the absorption at 425 nm. of the color formed during the reaction of nitric acid with pulp is a function of heating time, t, temperature, T, nitric acid concentration, c, and of sample size, m:

$$abs_{425\ nm.} = f(c,t,T,m) \qquad (3).$$

It is possible to derive an empirical equation expressing the absorption as a function of the four parameters. This could be achieved by properly designed factorial experiments. The derived equation could then be optimized to establish the optimum reaction conditions. However, this approach would in this particular case involve a vast amount of work, so it was decided to perform only a few experiments varying one parameter at a time and keeping the others constant. Aspen kraft and loblolly pine kraft pulps were used for these experiments.

Thirty-mg. samples of each were heated for increasing periods of time at 63, 70, and 75°C. with 50 ml. of 14% nitric acid, following the experimental procedure outlined above. In Fig. 14 and 15 are plotted the absorbance readings against reaction time. It is seen that the reaction rate increases with increasing temperature, the reaction rate of the pine being faster than that of the aspen. It is further noticed that the absorption decreases after a maximum is reached;

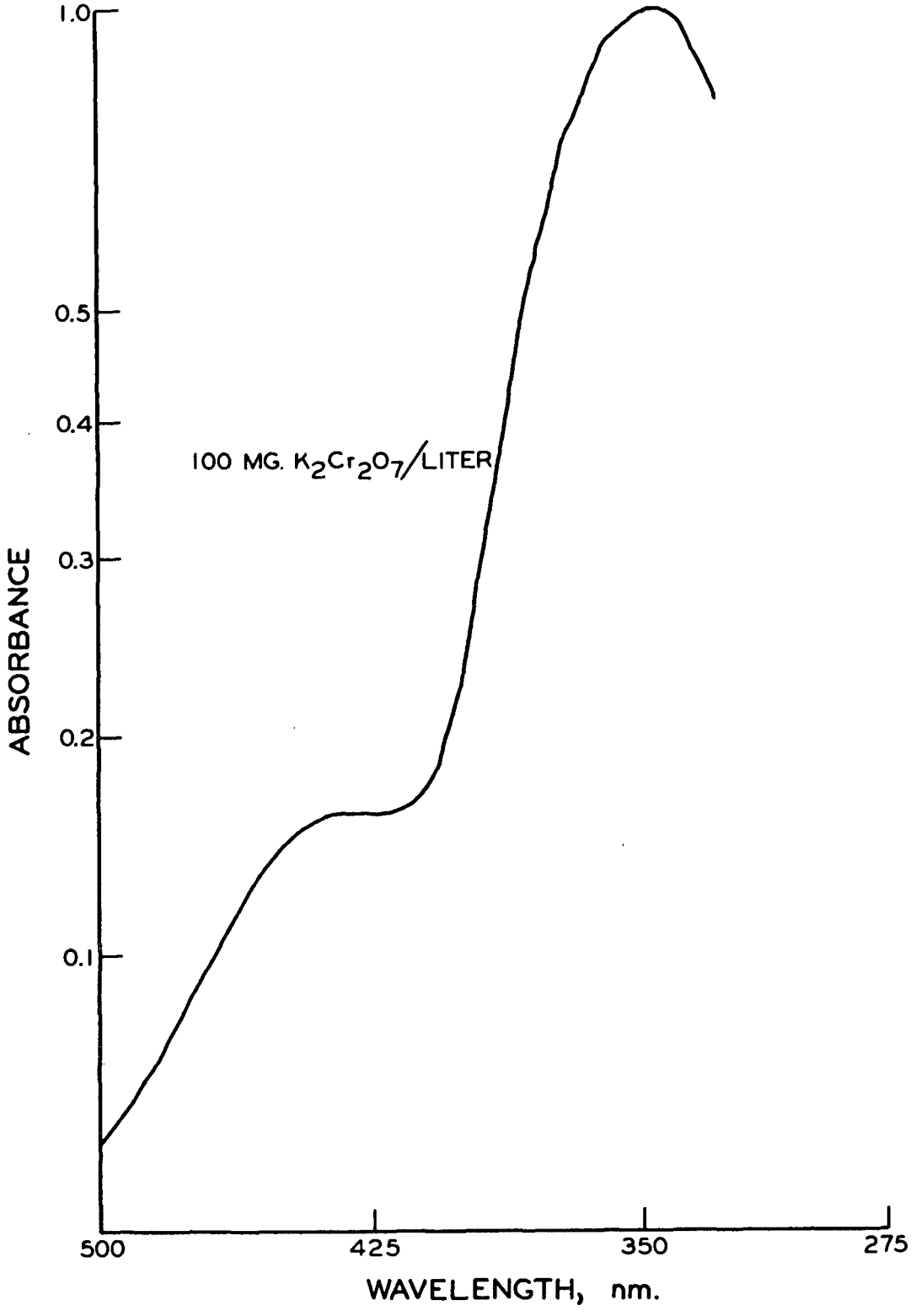

Figure 12. Absorbance Spectrum of Potassium Dichromate

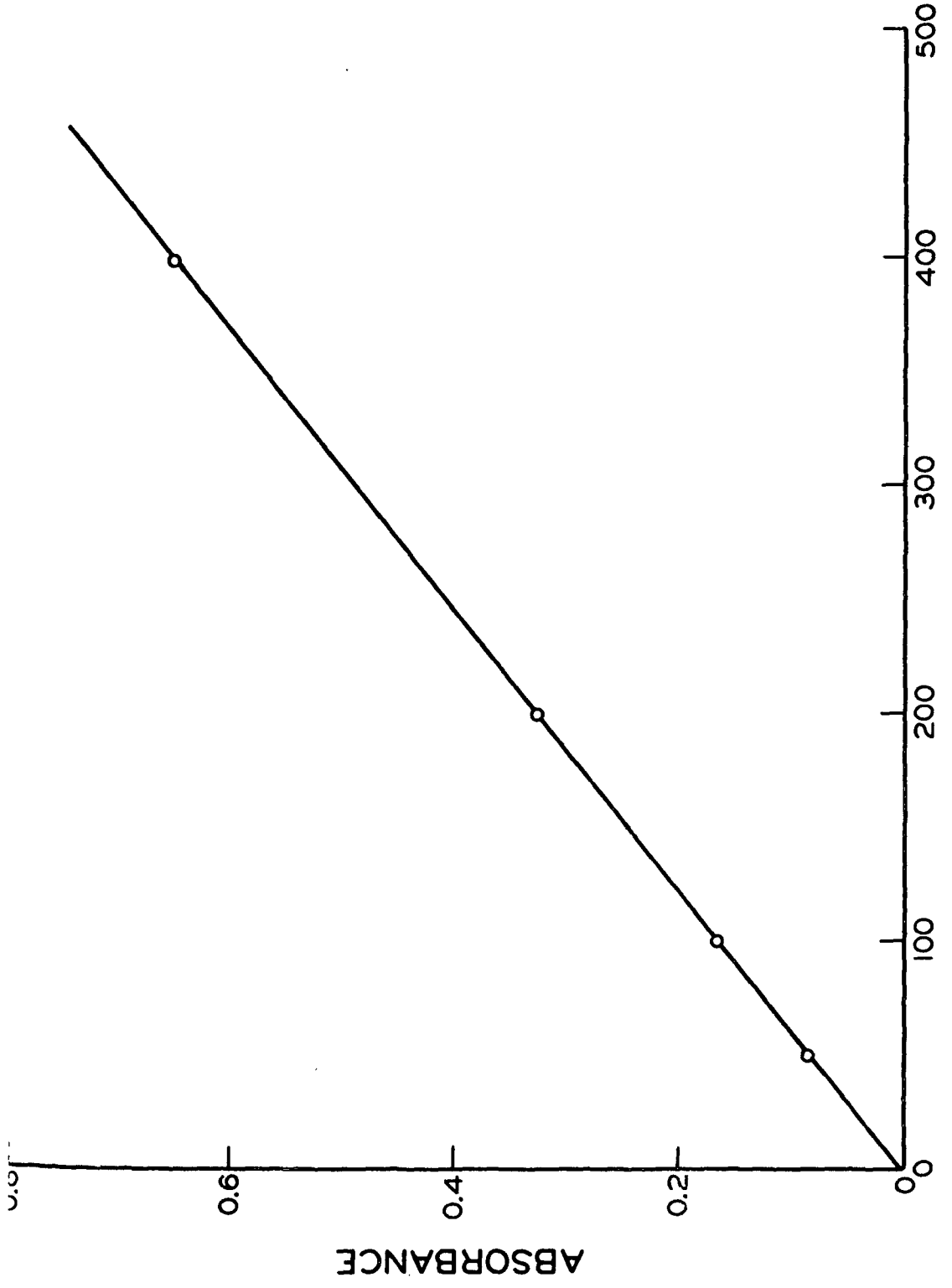

Figure 13. Reference Curve of Potassium Dichromate Standards at 425 nm.

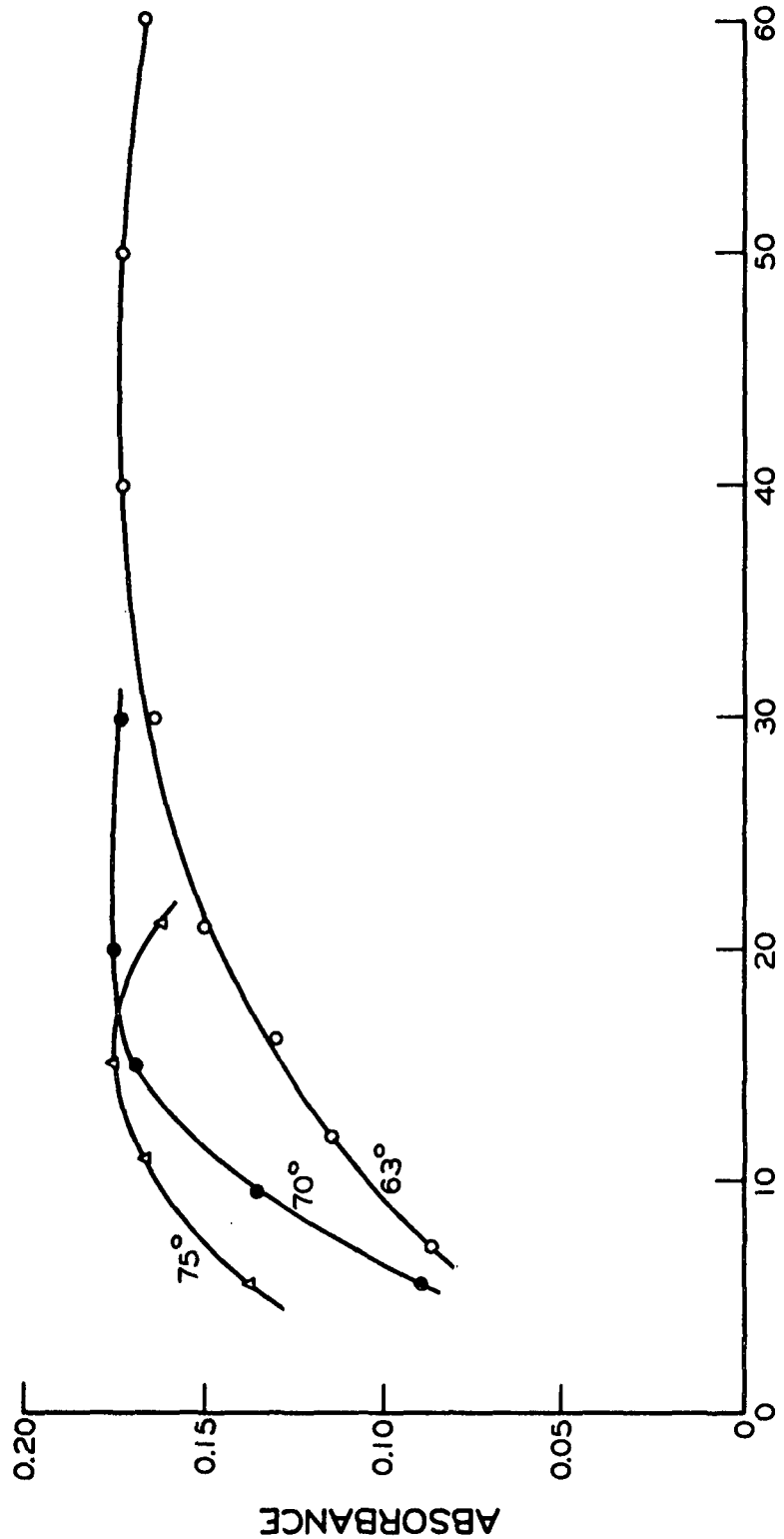

Figure 14. Absorbance of Aspen Pulp Extract at 425 nm. as a Function of Time and Temperature

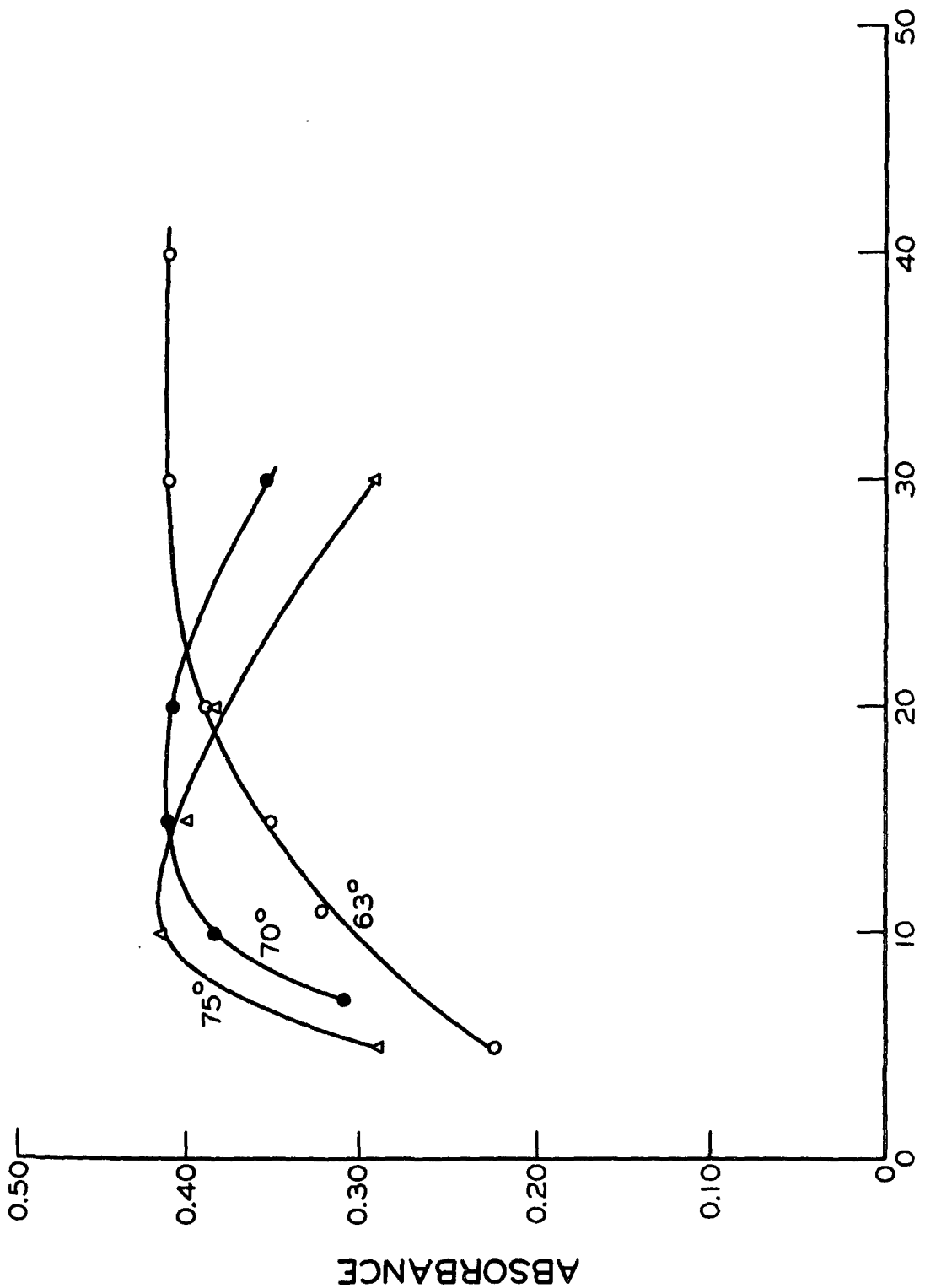

Figure 15. Absorbance of Loblolly Pine Pulp at 425 nm. as a Function of Time and Temperature

this decrease starts after a shorter time as the temperature increases. In Fig. 16 are shown the absorption spectra obtained from the aspen pulp when 30-mg. samples were heated with 14% nitric acid at 70°C. for increasing periods of time. These curves indicate that the absorbance maximum at 425 nm. passes through an intensity maximum, while the absorbance maximum at ca. 340 nm. increases in intensity with increasing reaction time. Further, the minimum around 400 nm. varies approximately parallel to the maximum at 425 nm. The wavelength at which the absorption is at minimum, however, varies. The ratios between the absorbance at 425 nm. and at ca. 400 nm. were calculated for all the experiments represented by Fig. 14 and 15, and are given in Table IX together with the corresponding absorbance values at 425 nm. The maximum values of these ratios coincide with those of the 425-nm. absorption, and the maximum ratio is the same for each kind of pulp.

A few experiments with 12 and 16% nitric acid showed that increasing concentration increased the reaction rate at a fixed temperature.

With 14% HNO_3 the absorbance does not increase in linear proportion to sample size, as shown in Fig. 17. However, within a range of $\pm$ 5 mg., the deviation from linearity is not significant.

As mentioned, the samples used for these experiments were ground to 40 mesh. Twenty and 80-mesh samples gave the same absorbance. When 30 mg. of the unground, air-dried pulps were analyzed, lower absorbances were obtained. However, when these were soaked in water overnight and analyzed the next day, the same absorbance values as for ground samples were obtained. This indicates that fibers in suspension would give the same absorbance as the ground samples.

The yellow color formed in this reaction is slightly sensitive to light. However, the absorbance does not decrease significantly within 10 minutes after

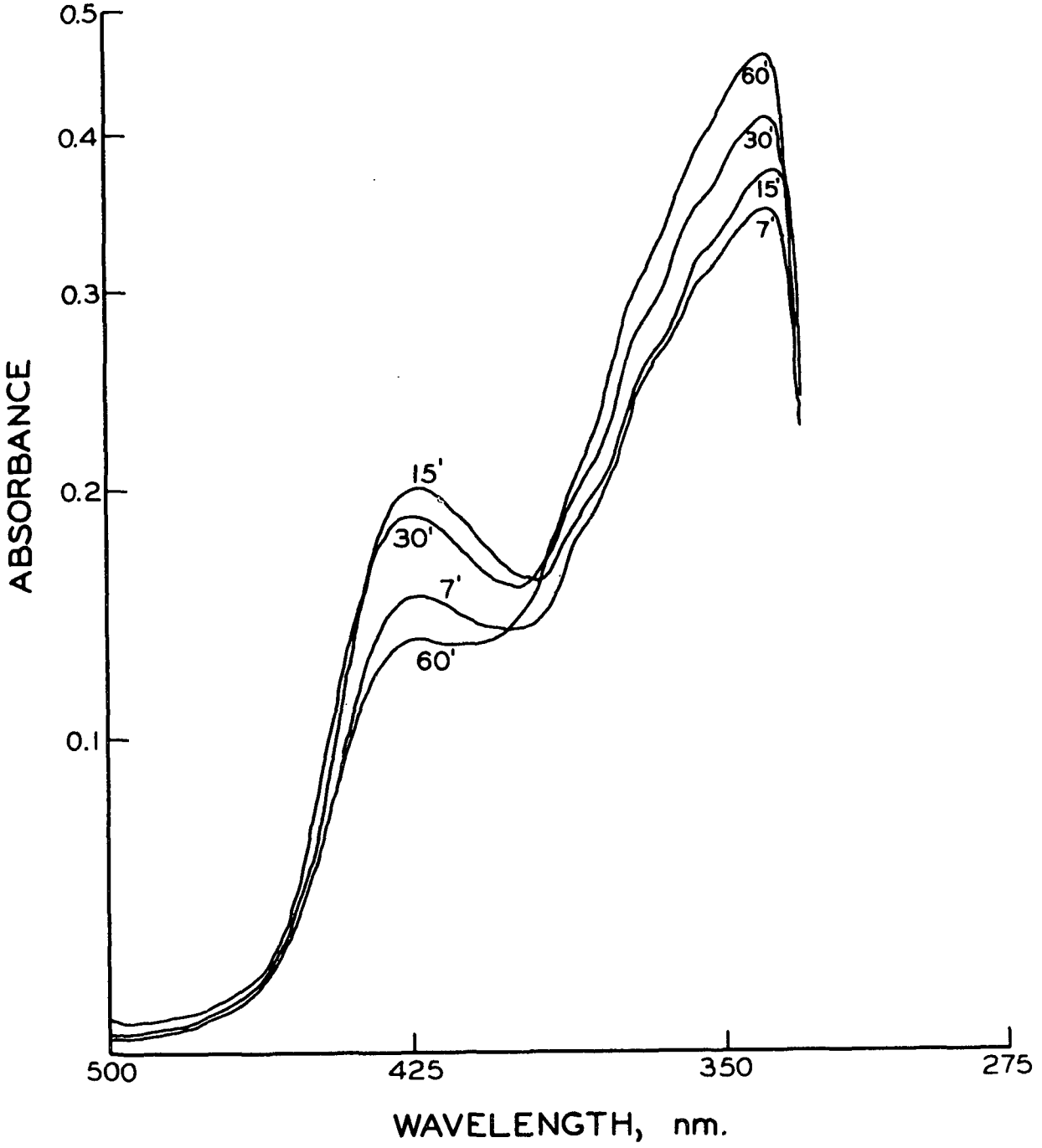

Figure 16. Absorbance Spectra of Aspen Pulp Extracts at 70°C. as a Function of Heating Time

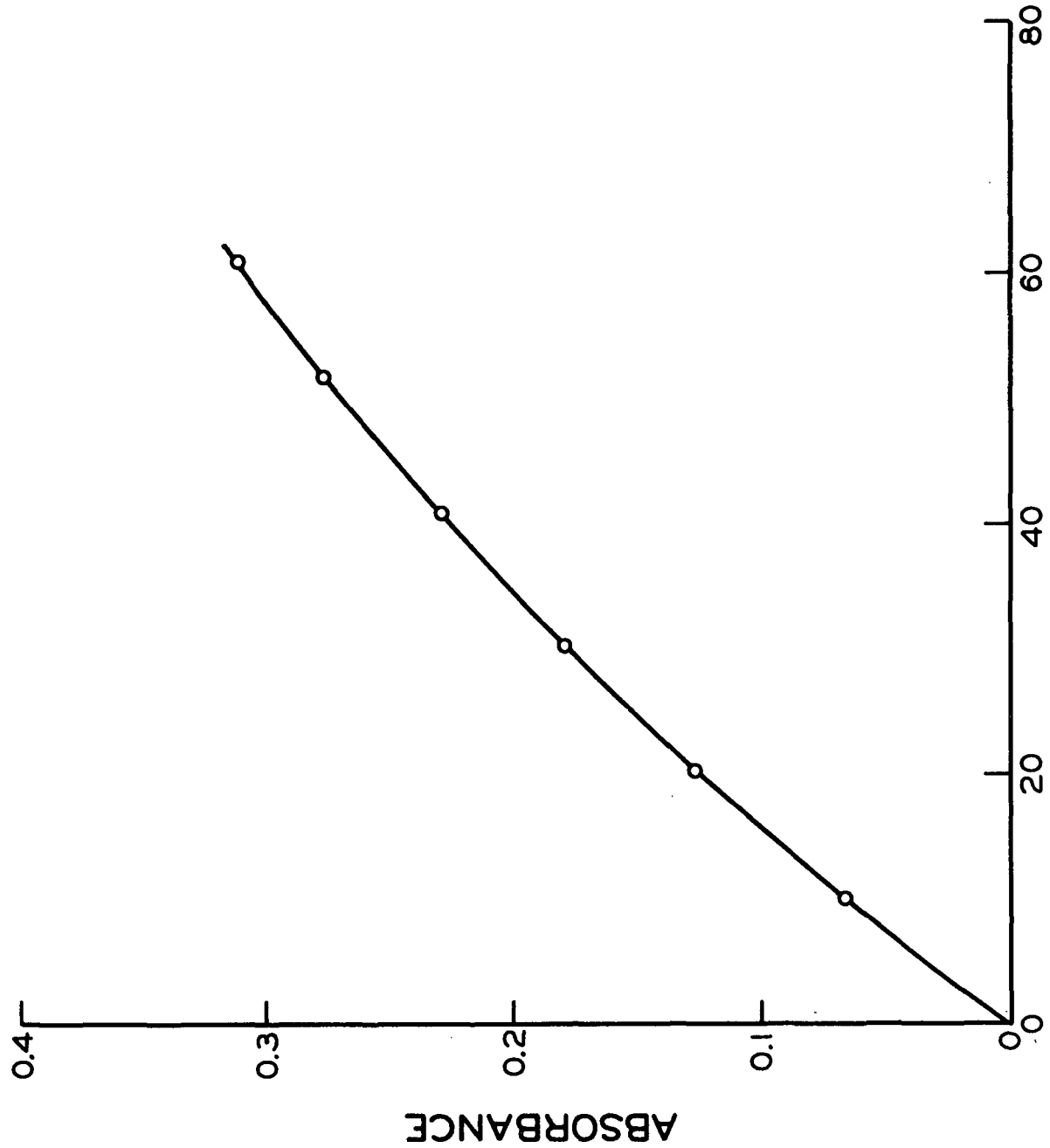

Figure 17. Abosrbance of Yellow Extract as a Function of Sample Size

TABLE IX

RATIOS OF MAXIMUM TO MINIMUM ABSORBANCES UNDER VARIOUS CONDITIONS

Sample and Reaction Time		Temperature, °C.	Absorption at 425 nm.	Ratio Max./Min.
Aspen	5	70	0.090	1.07
	10	70	0.137	1.23
	15	70	0.171	1.31
	20	70	0.180	1.34
	30	70	0.176	1.32
Aspen	6	75	0.138	1.16
	11	75	0.172	1.32
	15	75	0.178	1.33
	21	75	0.163	1.31
	32	75	0.138	1.21
Aspen	7	63	0.089	1.05
	12	63	0.115	1.15
	16	63	0.133	1.20
	21	63	0.152	1.26
	30	63	0.166	1.31
	40	63	0.176	1.33
	60	63	0.167	1.28
Loblolly	7	70	0.312	1.40
	10	70	0.384	1.54
	15	70	0.415	1.58
	20	70	0.404	1.54
	30	70	0.348	1.42
Loblolly	5	75	0.292	1.44
	10	75	0.414	1.58
	15	75	0.402	1.52
	20	75	0.386	1.44
	30	75	0.275	1.25
Loblolly	5	63	0.218	1.28
	11	63	0.317	1.45
	15	63	0.346	1.54
	20	63	0.380	1.56
	30	63	0.413	1.59
	40	63	0.408	1.56

the filtration is completed. When shielded from light the color is stable for at least one hour.

The results of these experiments indicate that a much more extensive study of the reaction between nitric acid and pulp would be desirable, and that it could possibly be developed into a general method for the measurement of residual lignin in pulp.

CONCLUSIVE STUDIES ON ANALYTICAL METHODS

It can be seen from the preceding section on initial experiments that of the many approaches and methods available upon which could be based an automated procedure for measuring degree of delignification, one involving direct use of the pulp itself has been selected for further study. Also, because of the promising results of the initial experiments on measurement of lignin in liquor, a deeper study of factors affecting these measurements seem warranted.

To supply known and defined samples of black liquor and of pulp for these further studies a series of cooks were made in a laboratory digester. The digester consisted of seven separate small pressure vessels attached to a rotating shaft, all of which are immersed in a constant-temperature oil bath during the cooking cycle. This design allows the removal of individual vessels at any selected time interval, and can result in the exposure of essentially seven cooks simultaneously to identical conditions. Since the temperature setting of the oil bath is changeable, this unit provides an excellent means of producing black liquor and pulp samples of a wide variety.

Commercial pulp samples were obtained from seven kraft mills, and represent a variety of pulping conditions and wood species. These were obtained to supplement the studies made with the pulp samples prepared in the laboratory multiunit digester.

LABORATORY COOKS

Table X gives the cooking conditions for the ten cooks made. In Cook VII, two units were used twice to obtain the time intervals desired. In all cooks the wood was in the form of "pin-chips" having a diameter of about

TABLE X

CONDITIONS OF MULTIUNIT DIGESTER COOKS

Charge: 20 g. o.d. wood

Cook No.	Wood Species	White Liquor Composition		Liquor-to-Wood Ratio	Digester Temperature, °C.	Cooking Times, min.
		Sulfidity, %	Effective Alkali, g./l. as Na_2O			
I	Loblolly pine	40	40	6:1	140	5, 15, 35, 75, 130, 190, 320
II	Loblolly pine	20	20	6:1	160	5, 15, 35, 75, 130, 190, 320
III	Aspen	33	29	10:1	165	15, 20, 25, 30, 35, 45, 80
IV	Aspen	33	52	10:1	165	15, 20, 25, 30, 35, 45, 80
V	Aspen	33	29	10:1	140	15, 40, 80, 130, 190, 250, 320
VI	Aspen	33	29	10:1	140	40, 50, 60, 70, 80, 90, 110
VII	Aspen	25	14	6:1	170	20, 25, 40, 50, 60, 70, 90, 110, 140
VIII	Black spruce	25	18	6:1	170	20, 40, 60, 70, 80, 100, 110
IX	Southern pine	25	18	6:1	170	25, 40, 60, 70, 80, 100, 110
X	Douglas-fir	25	18	6:1	170	25, 40, 60, 70, 80, 100, 110

TABLE XI

RESULTS OF MULTIUNIT DIGESTER COOKS

Cook	Cooking Time, min.	Yield, %	Yield, g.	Klason Lignin, % in pulp	Klason Lignin, tot. g.	Kappa Number
I	5	97.6	19.5	29.3	5.75	--
	15	82.1	16.4	29.2	4.80	--
	35	77.8	15.6	27.6	4.30	--
	75	72.4	14.5	25.9	3.80	--
	130	68.2	13.6	23.3	3.20	140
	190	63.3	12.7	19.4	2.45	128
	320	53.8	10.8	13.7	1.60	101
II	5	90.0	18.0	30.5	5.50	--
	15	80.1	16.0	29.7	4.80	--
	35	71.0	14.2	27.0	3.85	--
	75	66.0	13.2	22.9	3.05	146
	130	58.0	11.6	17.2	2.00	119
	190	53.8	10.8	13.6	1.45	93
	320	47.8	9.6	6.3	0.60	44
III	15	68.8	13.8	15.6	3.10	94
	20	62.2	12.4	11.1	2.20	77
	25	59.4	11.9	8.7	1.73	61
	30	55.8	11.2	6.0	1.20	43
	35	52.2	10.4	2.6	0.56	24
	45	49.8	10.0	1.7	0.30	13.5
	80	49.6	9.9	0.55	0.12	7.6
IV	15	63.6	12.7	14.4	2.82	89
	20	55.7	11.1	10.5	2.09	70
	25	52.8	10.6	7.7	1.46	52
	30	47.8	9.6	2.3	0.47	18
	35	47.8	9.6	2.0	0.38	14
	45	46.7	9.3	0.84	0.17	8
	80	44.8	9.0	0.44	0.09	4.8
V	15	76.7	15.3	18.6	2.82	--
	40	67.8	13.6	14.7	1.98	96
	80	61.3	12.3	9.8	1.20	66
	130	56.8	11.4	5.9	0.67	43
	190	53.5	10.7	3.0	0.32	25
	250	52.2	10.4	2.5	0.26	20
	320	51.0	10.2	1.2	0.12	13.5

TABLE XI (Continued)

RESULTS OF MULTIUNIT DIGESTER COOKS

Cook	Cooking Time, min.	Yield, %	Yield, g.	Klason Lignin, % in pulp	Klason Lignin, tot. g.	Kappa Number
VI	40	67.0	13.4	14.9	2.00	94
	50	65.2	13.0	12.8	1.68	79
	60	63.1	12.6	11.6	1.47	80
	70	62.1	12.4	10.6	1.32	73
	80	61.0	12.2	9.7	1.18	67
	90	60.2	12.0	8.9	1.07	65
	110	58.7	11.7	7.2	0.84	55
VII	20	70.0	14.0	14.4	2.01	96
	25	67.3	13.5	12.8	1.71	89
	40	61.5	12.3	8.0	1.20	55
	50	60.7	12.1	6.7	0.81	47
	60	58.3	11.7	5.0	0.58	36
	70	57.9	11.6	4.1	0.47	31
	90	55.5	11.1	2.3	0.25	19
	110	55.4	11.1	1.8	0.19	17
	140	54.5	10.9	1.5	0.16	12.6
VIII	20	72.8	14.8	25.4	3.66	151
	40	64.1	12.8	21.2	2.72	132
	60	57.5	11.5	15.4	1.76	106
	70	56.8	11.4	14.3	1.63	99
	80	53.4	10.7	11.3	1.21	80
	100	50.3	10.1	8.9	0.80	65
	110	51.8	10.4	9.1	0.95	66
IX	25	70.0	14.0	23.7	3.32	140
	40	61.2	12.2	21.7	2.67	135
	60	56.5	11.3	16.2	1.83	109
	70	54.3	10.9	14.7	1.60	101
	80	52.8	10.6	13.7	1.44	94
	100	48.6	9.7	8.7	0.85	62
	110	48.8	9.8	9.8	0.95	65
	25	63.4	12.7	24.7	3.14	135
	40	57.9	11.6	19.6	2.26	126
	60	52.5	10.5	16.3	1.71	109
	70	51.0	10.2	13.1	1.34	91
	80	49.0	9.8	12.7	1.24	82
	100	47.3	9.5	9.6	0.91	66
	110	46.5	9.3	9.5	0.89	62

TABLE XII

ANALYTICAL DATA ON COMMERCIAL PULP SAMPLES

Mill No.	Sample No.	Kappa No.	Klason Lignin, %
	1	29.2	3.85
	2	25.2	3.35
	3	25.6	3.40
	4	31.4	4.10
	5	31.4	4.05
	6	20.0	2.30
	7	30.6	3.90
1	8	30.7	3.75
	9	30.1	3.80
	10	28.1	3.75
	11	27.2	3.40
	12	31.3	3.70
	13	28.4	3.35
	14	25.8	3.55
	15	28.6	4.00
	16	27.9	3.60
	17	27.4	3.50
	1	64.1	9.75
	2	56.0	8.85
	3	53.0	8.40
	4	65.4	9.60
	5	53.0	7.60
	6	63.7	10.35
2	7	67.1	10.60
	8	53.6	8.20
	9	60.0	9.30
	10	54.6	8.85
	11	73.8	11.60
	12	55.8	9.15
	13	46.7	7.45
	14	68.5	11.10
	1	29.9	4.70
	2	32.7	5.25
	3	32.6	5.00
	4	30.9	4.75
	5	28.1	4.45
3	6	26.1	4.20
	7	35.3	5.50
	8	37.6	6.05
	9	34.8	5.45
	10	29.7	4.75
	11	28.5	4.65

Mill No.	Sample No.	Kappa No.	Klason Lignin, %
	1	18.3	2.90
	2	25.8	3.95
	3	27.3	4.05
	4	42.1	6.60
	5	57.6	9.00
4	6	23.7	3.55
	7	29.5	4.20
	8	29.2	4.20
	9	29.6	4.25
	10	27.2	4.05
	11	25.0	3.75
	12	22.3	3.40
	1	52.2	7.70
	2	52.9	7.75
	3	41.7	6.25
	4	38.8	5.85
	5	48.7	7.15
5	6	55.9	8.20
	7	63.3	9.25
	8	50.2	7.50
	9	54.7	7.55
	10	50.1	7.45
	11	39.2	5.80
	12	51.2	7.40
	1	41.0	5.95
	2	41.0	6.10
	3	40.1	5.80
	4	42.1	6.35
	5	43.4	6.45
6	6	46.3	7.15
	7	43.6	6.75
	8	39.1	5.70
	9	37.5	5.40
	10	38.7	5.60
	11	36.8	5.45
	12	37.3	5.40
	1	99.4	14.80
	2	106	17.45
	3	91.7	13.65
	4	90.3	13.40
	5	98.1	17.20
7	6	103	15.90
	7	110	17.25
	8	103	15.60
	9	109	16.95
	10	114	17.45
	11	104	15.70
	12	103	15.40

would still represent the time period over which the samples were taken, but would reduce the number of analytical determinations required. Thus, all of the samples from all of the mills are not represented in Table XII.

The available cooking data are presented in Table XIII.

TABLE XIII

COOKING DATA FOR COMMERCIAL PULP SAMPLES

Mill	Wood Species	Max. Temp., °F.	White Liquor Composition: Eff. Alk., lb./cu. ft. as Na_2O	White Liquor Composition: Sulfidity, %	Total Liquor-to-Wood Ratio
1	Mixed lodgepole, ponderosa, and jack pine	360	5.8	36	--
2	Douglas-fir	355	5.7	24	3:1
3	Douglas-fir + some pine	348	5.3	25	3.5:1
4	Loblolly, slash, and longleaf pine mixture	343	4.9	25	--
5	Mixed pines	337	6.0	25	--
6	Mix of Douglas-fir, West. hemlock, pine, spruce and larch	340	4.2	23	--
7	Southern pines	310	5.7	27	3.4

LIGNIN-IN-LIQUOR

All black liquor samples from the laboratory cooks were subjected to three methods of analysis for lignin: (a) the U.V. difference method at 300 nm., (b) the Pearl-Benson colorimetric method, and (c) direct measurement of absorbance at 280 nm. In all these methods, Indulin A standards were prepared and the black liquor lignin concentrations were read against Indulin A calibration curves. These results are given in Table XIV.

TABLE XIV

RESULTS OF LIGNIN ANALYSIS IN BLACK LIQUORS FROM LABORATORY COOKS

Cook	Cooking Time, min.	Lignin in Liquor, grams: Pearl-Benson	Δ-300 nm.	280 nm.
I	5	0.18	0.24	0.24
	15	1.04	1.04	1.04
	35	1.92	1.98	1.86
	75	2.88	2.88	2.76
	130	3.84	3.72	3.65
	190	4.80	4.62	4.38
	320	5.94	5.58	5.22
II	5	0.48	0.48	0.48
	15	1.38	1.56	1.44
	35	2.82	2.88	2.52
	75	4.38	4.38	3.90
	130	5.64	5.51	5.10
	190	5.94	6.00	5.45
	320	7.40	7.26	6.72
III	15	2.14	1.54	0.94
	20	3.00	2.62	2.64
	25	3.44	3.44	2.98
	30	4.10	3.90	3.44
	35	4.60	4.46	3.94
	45	5.30	5.48	4.64
	80	5.92	6.06	5.18
IV	15	2.24	1.76	1.90
	20	3.16	2.80	2.64
	25	3.80	3.80	3.26
	30	4.72	4.74	4.12
	35	5.02	5.20	4.36
	45	5.90	6.06	4.96
	80	6.50	6.56	5.64
V	15	1.32	1.00	1.20
	40	2.70	2.12	2.00
	80	4.24	3.90	3.02
	130	5.10	5.11	3.64
	190	5.90	6.10	4.14
	250	6.30	6.40	4.44
	320	6.30	6.40	4.60
VI	40	2.50	2.10	2.12
	50	3.00	2.50	2.12
	60	3.50	2.90	2.64
	70	3.70	3.40	2.88
	80	3.90	3.50	3.02
	90	4.10	3.90	3.16
	110	4.50	4.30	3.42
VII	20	2.14	2.39	1.80
	25	2.42	2.90	2.10
	40	3.00	3.58	2.60
	50	3.75	4.36	3.07
	60	4.20	4.48	3.42
	70	4.30	4.54	3.37
	90	4.88	5.33	3.76
	110	4.92	5.32	3.83
	140	5.11	5.28	3.93
VIII	20	2.21	2.38	2.19
	40	3.62	3.66	3.51
	60	4.94	4.68	4.60
	70	5.07	4.95	4.80
	80	5.79	5.38	5.31
	100	6.37	6.01	6.00
	110	6.19	5.70	5.67
IX	25	2.19	2.54	2.55
	40	3.26	3.57	3.68
	60	4.21	4.24	4.46
	70	4.68	4.69	4.97
	80	4.82	4.80	5.14
	100	5.91	5.59	5.97
	110	4.92	4.80	5.15
X	25	3.20	3.44	3.63
	40	4.41	4.51	4.84
	60	5.37	5.24	5.77
	70	5.65	5.52	6.00
	80	6.08	5.94	6.30
	100	6.48	6.05	6.75
	110	6.83	6.60	6.75

The mean lignin content of the liquors from each kind of wood was calculated for each of the three methods, and the differences in the mean values were tested for significance by the paired comparison technique. In Table XV are given the t-values calculated for the differences in mean values together with the table t-values for the 95 and 99% significance levels. According to statistical theory, a significant difference in mean values exists when the calculated t-value exceeds the 95%-level t-value. By inspection of Table XV it is seen that the difference between the Pearl-Benson method and the method utilizing the difference absorption at 300 nm. is not significant for any kind of wood. However, when the method utilizing the absorption at 280 nm. is compared with the two other methods, a significant difference is shown to exist. Thus, since the Pearl-Benson method is shown to agree with the difference method, it was decided to use the results from the former method for estimating the correlation between the amount of lignin found in the liquor and the lignin content of the pulp.

A negative correlation would be expected between these two forms of lignin. Regression lines of the lignin in pulp upon the lignin in the liquor were calculated for each cook and for each kind of wood. The corresponding correlation coefficients and the respective standard errors of the estimates of the lignin in the pulp were also calculated, together with the relative average standard errors. In Table XVI are given the calculated results, and in Fig. 18 and 19 are drawn the regression lines.

Theoretically, the sum of lignin in pulp and in liquor should be constant and equal to the original lignin content of the wood. However, since lignin in the liquor is determined relative to a standard (Indulin A) not derived from the same source as lignin in the pulp (Klason lignin), the lignin

TABLE XV

PAIRED COMPARISON OF METHODS FOR DETERMINING LIGNIN IN LIQUOR

Cooks I-X

Cook No.	Wood	N	Pearl-Benson vs. Δ-300 nm.		Pearl-Benson vs. 280 nm.		Δ-300 nm. vs. 280 nm.		Table t-Values	
			$\bar{d}$	t	$\bar{d}$	t	$\bar{d}$	t	95%	99%
I-II	Loblolly pine	14	-0.042	1.22	-0.277	3.71	-0.241	4.29	2.16	3.01
III-VII	Aspen	37	-0.040	0.70	-0.830	12.27	-0.74	6.10	2.03	2.71
VIII	Black spruce	7	-0.204	2.20	-0.301	4.34	+0.097	3.67	2.45	3.71
IX	Southern pine	7	+0.040	0.42	+0.26	5.74	+0.240	4.54	2.45	3.71
X	Douglas-fir	7	-0.103	1.11	+0.29	4.24	+0.391	5.38	2.45	3.71
I-X	All woods	72	-0.055	1.73	+0.288	12.85	-0.362	6.70	2.00	2.65

TABLE XVI

REGRESSION LINES OF LIGNIN IN PULP ON LIGNIN IN LIQUOR (LABORATORY COOKS)

Cook No.	Wood	Regression Line	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %
III	Aspen	$L_p = 4.61-0.807\ L_\ell$	-0.977	0.24	18
IV	Aspen	$L_p = 4.18-0.695\ L_\ell$	-0.976	0.24	22
V	Aspen	$L_p = 4.02-0.520\ L_\ell$	-0.986	0.18	17
VI	Aspen	$L_p = 3.45-0.578\ L_\ell$	-0.980	0.10	7.5
VII	Aspen	$L_p = 3.17-0.609\ L_\ell$	-0.996	0.07	8.5
I + II	Loblolly pine	$L_p = 5.80-0.740\ L_\ell$	-0.987	0.24	7
VIII	Black spruce	$L_p = 5.01-0.652\ L_\ell$	-0.966	0.26	14
IX	Southern pine	$L_p = 4.81-0.700\ L_\ell$	-0.962	0.24	13
X	Douglas-fir	$L_p = 5.04-0.627\ L_\ell$	-0.972	0.19	12

content of the liquor should be multiplied by a factor b in order to convert this value to Klason lignin. The formula correlating these two forms of lignin is:

$$y + bx = a \qquad (4)$$

or

$$y = a - bx \qquad (5)$$

where x and y are the lignin contents of liquor and pulp, respectively, a is the lignin content of the wood, and b is the conversion factor. It might be expected that this factor is determined mainly by the wood species. Thus, the regression

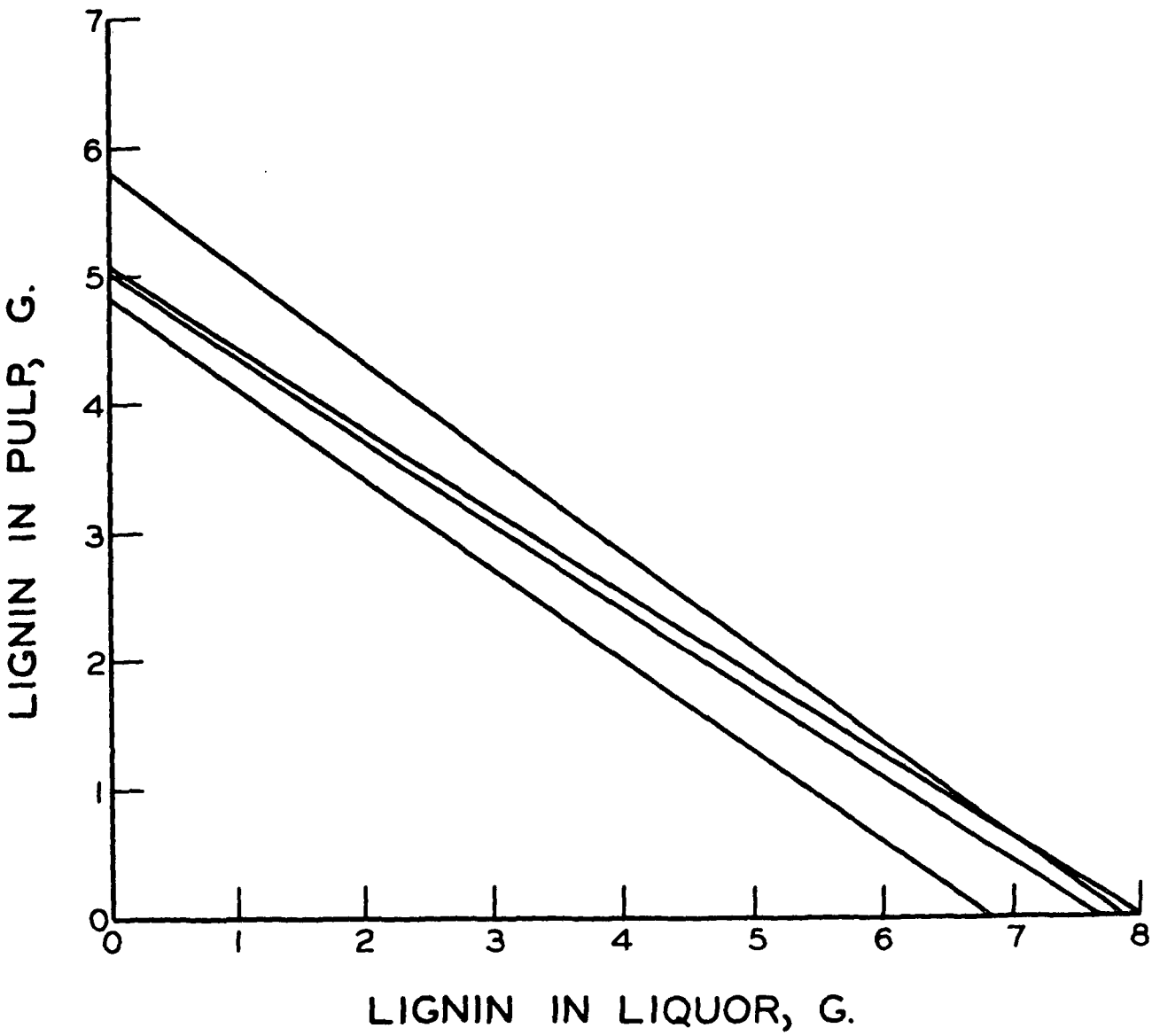

Figure 18. Regression Lines of Lignin in Liquor Upon Lignin (Klason) in Pulp for Laboratory Cooks of Softwood

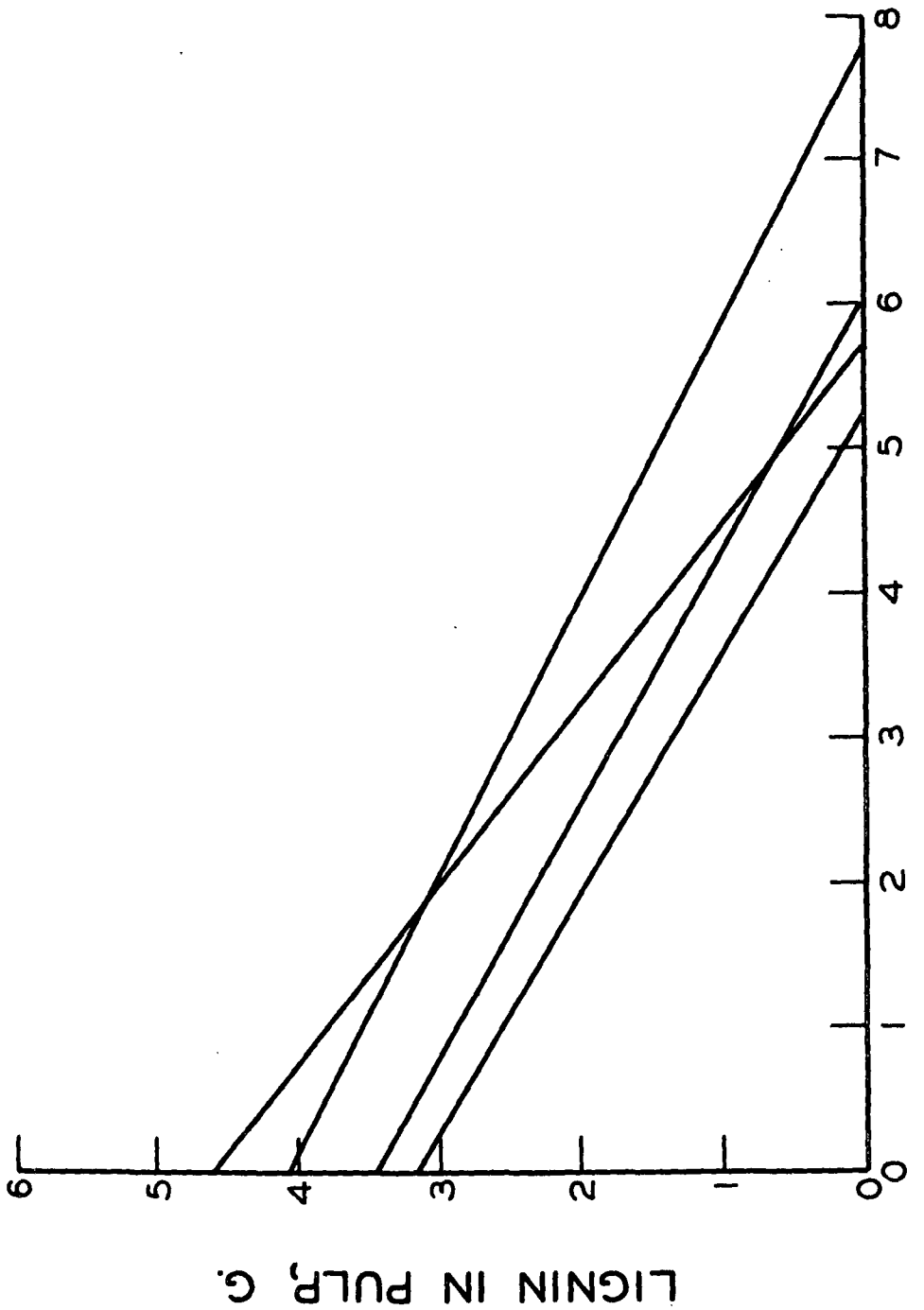

Figure 19. Regression Lines of Lignin in Liquor Upon Lignin (Klason) in Pulp for Laboratory Cooks of Aspen

lines for cooks using the same wood, even under different conditions, should be similar. From Table X it is seen that the aspen cooks II-VII were performed at varying liquor composition, temperature, and liquor-to-wood ratio. Since the lignin content of the aspenwood is 3.93 g. (in 20 g. wood), the theoretical regression line is: $\underline{y} = 3.93 - \underline{b}\underline{x}$. The regression lines shown in Table XVI and Fig. 19 indicate that the cooking conditions, contrary to expectations, have a pronounced influence on the regression lines. As a consequence, the regression equation must be determined for each set of conditions. The correlation coefficients, however, show that a close correlation exists between the two forms of lignin, but the standard error and the relative error of the estimate indicate that the precision in estimation of lignin in liquor is rather low, the mean relative error being $\pm$ 12%. It is further seen that for the other cooks, which were performed under identical conditions but using different wood species, the relative error of the estimates is of the same order of magnitude as for the aspen cooks. Thus, if a change of 10% in lignin content in the liquor is measured, it need not reflect a significant change in the lignin content (or "hardness") of the pulp. A calculation of the same parameters based on the results obtained by the 280-nm. absorption method (not shown here) does not give improved results. Consequently, these results indicate that measurement of lignin in the liquor is not an accurate indirect measure of the degree of delignification of the pulp.

LIGNIN IN PULP

Since the initial experiments with the nitric acid method showed promise of its yielding good results, the procedure was applied to all of the pulps made in the laboratory cooks and to the commercial pulp samples. It also seemed appropriate at this time to name and define the results from this procedure. Following

the precedent of the "Kappa" no., the name "Nu number" was chosen to identify the method, and its definition follows:

Equipment

100-ml. beaker

50-ml. pipet

18-cm. test tube, actinic glass

Whatman filter paper no. 40, 9 cm.

constant-temperature bath

spectrophotometer with matched 10-mm. silica cells

Reagent

14% nitric acid: Dilute 200 ml. concd. nitric acid (reagent grade) to 1 liter with distilled water.

Procedure

Weigh out exactly about 30 mg. of ground pulp (40-mesh) on an analytical balance in a 100-ml. beaker. Add 50 ml. of 14% nitric acid and heat the beaker with its contents on the water bath set at 70°C. for a suitable period of time given by the kind of pulp to be analyzed (see below). Remove the beaker, filter immediately into the test tube, and measure the absorption at 425 nm. within 5 minutes against a blank made of 14% nitric acid.

Prepare a calibration curve at 425 nm. from solutions of 50, 100, 200, and 400 mg. $K_2Cr_2O_7$ per liter.

Read the sample absorbance value at 425 nm. against the calibration curve and calculate the Nu number from formula (6):

$$Nu = \frac{Mw}{30} \qquad (6)$$

where M is the number of milligrams of $K_2Cr_2O_7$ read from the calibration curve and w is the milligrams of pulp used.

Laboratory Pulps

During initial application of the nitric acid method it was found that the heating time giving maximum absorption at 425 nm. varied with the kind of pulp, and also if the pulps were obtained from laboratory cooks or from commercial samples. Thus, the heating time for the softwood laboratory pulps was 20 min., while for most of the mill pulps the heating time was 30-40 min. at the same temperature. Therefore, each time a new series of pulp was analyzed, a reaction rate curve was established to determine the proper heating time. In Fig. 20 are shown the reaction rate curves for the laboratory pulps, and in Fig. 21 the corresponding curves for the mill pulps.

It was further found that the following variations in conditions had little influence on the results: T = 70 ± 1°C., conc.. HNO_3 = 14 ± 1%, sample wt. = 30 ± 5 mg., reaction time = ± 3 min. The results, giving the Nu number of both the commercial pulps and those produced in the laboratory cooks, are given in Table XVII.

It is known that a straight-line relationship exists between % Klason lignin and Kappa number for pulps with yields below 70%, and that this line passes through the point of zero lignin-zero Kappa number. According to Tasman and Berzins (39), this relationship is given with reasonable accuracy by Equation (7):

$$\% \text{ Klason lignin} = 0.13 \text{ Kappa number} \qquad (7).$$

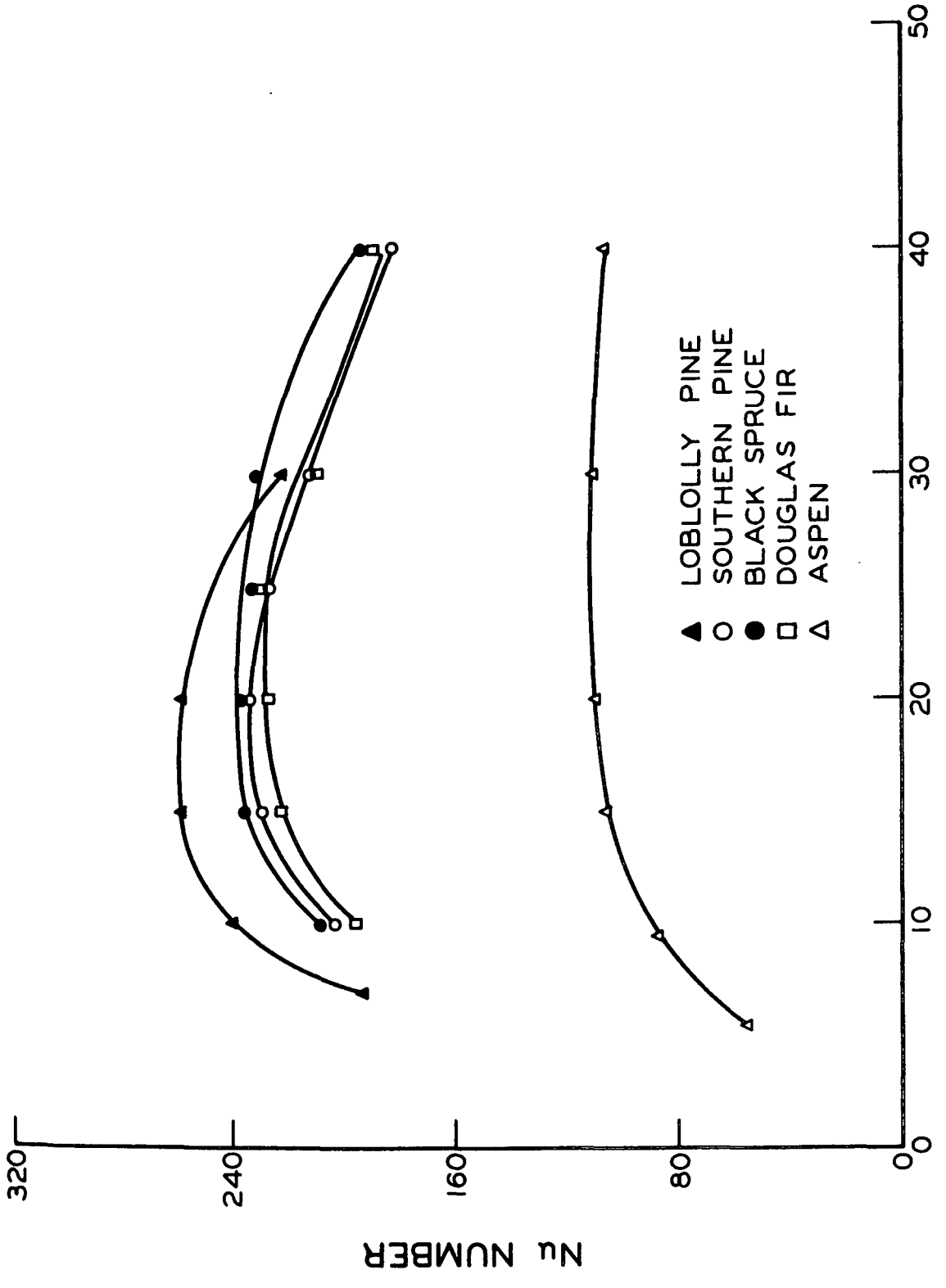

Figure 20. Reaction Rate Curves of Experimental Pulps with 14% HNO_3 at 70°C.

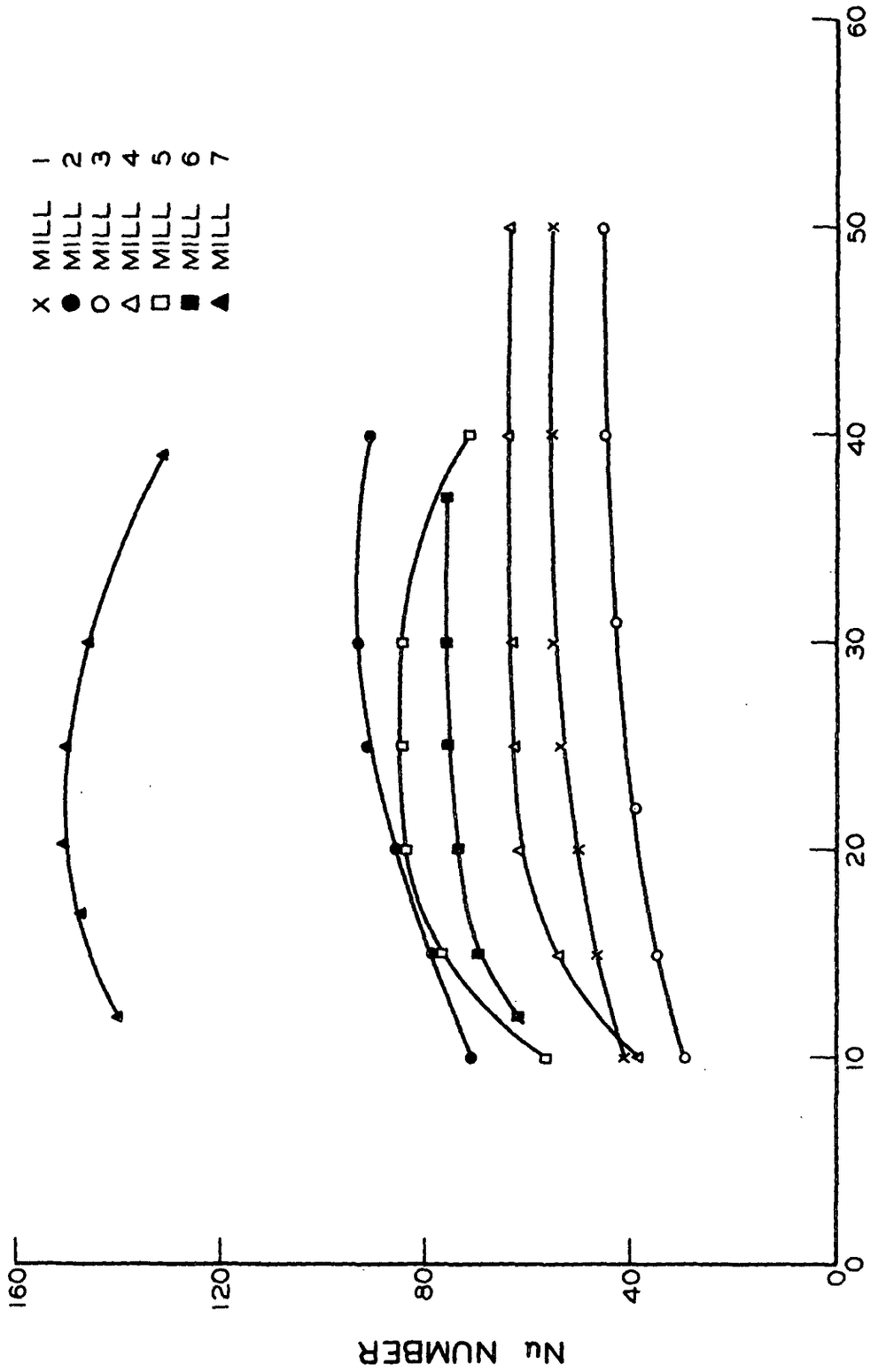

Figure 21. Reaction Rate Curves of Commercial Pulps with 14% HNO_3 at 70°C.

TABLE XVII

Nu NUMBERS OF COMMERCIAL PULPS AND LABORATORY PRODUCED PULPS

Laboratory Pulps			Commercial Pulps		
Cook	Cooking Time, min.	Nu Number	Mill	Sample No.	Nu Number
	5	--		1	50
	15	--		2	44
	35	--		3	44
I	75	--		4	55
	130	325		5	52
	190	282		6	35
	320	219		7	54
			1	8	53
	5	--		9	51
	15	--		10	50
	35	--		11	45
II	75	334		12	50
	130	259		13	48
	190	205		14	43
	320	100		15	47
				16	45
	15	140		17	47
	20	108			
	25	88		1	98
III	30	64		2	88
	35	34		3	84
	45	17		4	98
	80	7.5		5	85
				6	100
	15	134	2	7	104
	20	109		8	87
	25	80		9	96
IV	30	28		10	88
	35	24		11	110
	45	12		12	89
	80	7.2		13	75
				14	106
	15	151			
	40	136		1	47
	80	95		2	51
V	130	65		3	50
	190	35		4	49
	250	28		5	46
	320	17	3	6	44
				7	55
	40	131		8	59
	50	114		9	54
I	60	110		10	48
	70	104		11	46
	80	96			
	90	[illegible]			

TABLE XVII (Continued)

Nu NUMBERS OF COMMERCIAL PULPS AND LABORATORY PRODUCED PULPS

Laboratory Pulps			Commercial Pulps		
Cook	Cooking Time, min.	Nu Number	Mill	Sample No.	Nu Number
	20	131		1	32
	25	122		2	37
	40	85		3	41
	50	71		4	62
VII	60	55		5	80
	70	45	4	6	37
	90	24		7	40
	110	18		8	39
	140	12		9	39
				10	38
	20	326		11	32
	40	299		12	31
	60	237			
VIII	70	224		1	81
	80	188		2	82
	100	140		3	67
	110	147		4	66
				5	73
	25	314	5	6	83
	40	300		7	90
	60	234		8	78
IX	70	213		9	79
	80	205		10	76
	100	139		11	60
	110	143		12	75
	25	318		1	69
	40	277		2	74
	60	233		3	68
X	70	209		4	75
	80	188		5	78
	100	140	6	6	85
	110	133		7	76
				8	71
				9	65
				10	67
				11	64
				12	61
				1	151
				2	161
				3	145
				4	143
				5	155
			7	6	163
				7	170
				8	159
				9	158
				10	173
				11	163
				12	161

If the Nu number method is a true measure of the lignin content of pulp, a similar straight-line relationship between it and Kappa number and Klason lignin would be expected.

The regression relationship between two correlated variables is defined by Equation (8):

$$y = a + bx \tag{8}$$

where x and y are the independent and dependent variables, respectively, and a is the intercept of the straight line with the y-axis. The coefficient of regression, b, is a measure of the slope of the curve. If the regression line passes through the origin, a is equal to zero, and the relationship between the two variables is given by b only. In this case the regression coefficient is found by simply calculating the ratio between the mean values.

Using the data given in Tables XI and XVII, the regression relationships for the laboratory cooks of Klason lignin on the Kappa and Nu numbers, and Kappa number on Nu number, were calculated for each kind of wood as well as for all softwoods. The corresponding correlation coefficients and the respective standard errors of the estimates were also calculated together with the relative average standard errors. The standard error of the estimate is defined by the standard deviation of the difference between the values actually found and the values calculated from the equation of the regression line. The relative average standard error is the standard error's percentage of the mean value. The standard error of the estimates and the relative average standard errors were also calculated based on the relationship $y = bx$. The calculated data are given in Tables XVIII, XIX, and XX.

TABLE XVIII

REGRESSION RELATIONSHIPS OF KLASON LIGNIN ON Kappa NUMBER

(Laboratory cooks)

Wood	No. of Tests	Regression Lines	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %	Range of Lignin, %
Loblolly pine	7	% KL = -1.90 + 0.168 Kappa	0.985	0.94	5.60	% KL = 0.151 Kappa	1.09	6.55	6-23
Black spruce	7	% KL = -3.72 + 0.186 Kappa	0.995	0.57	3.77	% KL = 0.152 Kappa	0.94	6.22	9-25
Southern pine	7	% KL = -2.80 + 0.182 Kappa	0.991	0.68	4.39	% KL = 0.154 Kappa	1.04	6.71	9-24
Douglas-fir	7	% KL = -2.42 + 0.184 Kappa	0.972	1.20	7.95	% KL = 0.158 Kappa	1.40	9.27	9-25
All softwoods	28	% KL = -2.71 + 0.180 Kappa	0.986	0.80	5.04	% KL = 0.153 Kappa	1.12	7.06	6-25
Aspen	36	% KL = -0.86 + 0.162 Kappa	0.997	0.32	4.55	% KL = 0.144 Kappa	0.38	5.40	0.5-15

TABLE XIX

REGRESSION RELATIONSHIPS OF KLASON LIGNIN ON Nu NUMBERS

(Laboratory cooks)

Wood	No. of Tests	Regression Lines	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %	Range of Lignin, %
Loblolly pine	7	% KL = -1.60 + 0.074 Nu	0.995	0.52	3.20	% KL = 0.0675 Nu	0.72	4.32	6-23
Black spruce	7	% KL = -4.11 + 0.086 Nu	0.987	1.02	7.54	% KL = 0.0678 Nu	1.07	7.75	9-25
Southern pine	7	% KL = -2.50 + 0.081 Nu	0.996	0.46	3.00	% KL = 0.0702 Nu	0.85	5.48	9-24
Douglas-fir	7	% KL = -2.12 + 0.080 Nu	0.985	0.90	5.96	% KL = 0.0710 Nu	1.02	6.75	9-25
All softwoods	28	% KL = -2.60 + 0.080 Nu	0.991	0.72	4.54	% KL = 0.0690 Nu	0.94	7.06	6-25
Aspen	36	% KL = -0.73 + 0.111 Nu	0.996	0.34	4.83	% KL = 0.101 Nu	0.42	5.95	0.5-15

TABLE XX

REGRESSION RELATIONSHIPS OF Kappa ON Nu NUMBER

(Laboratory cooks)

Wood	No. of Tests	Regression Lines	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %
Loblolly pine	7	Kappa = 1.60 + 0.440 Nu	0.998	2.83	2.58	Kappa = 0.447 Nu	3.03	2.75
Black spruce	7	Kappa = 2.41 + 0.432 Nu	0.997	2.93	2.93	Kappa = 0.444 Nu	3.28	3.28
Southern pine	7	Kappa = 3.70 + 0.438 Nu	0.997	2.15	2.13	Kappa = 0.450 Nu	2.45	2.43
Douglas-fir	7	Kappa = 3.55 + 0.428 Nu	0.992	3.50	3.66	Kappa = 0.447 Nu	3.66	3.85
All softwoods	28	Kappa = 2.18 + 0.438 Nu	0.997	2.28	2.24	Kappa = 0.447 Nu	2.32	2.28
Aspen	36	Kappa = 0.84 + 0.686 Nu	0.996	1.95	4.00	Kappa = 0.700 Nu	2.00	4.10

Regression Relationships of Klason Lignin on Kappa and Nu Number

From Tables XVIII and XIX it is seen that the regression lines of Klason lignin on both the Kappa and Nu numbers show a negative intercept with the y-axis. This means that a pulp with no Klason lignin still possesses a positive Kappa and Nu number. In the case of the Kappa number, this could be explained as being due to slight oxidation of the carbohydrates in the pulp. It can be shown statistically that these intercepts are highly significant, thus indicating that the line passing through the origin is significantly different from the calculated regression line. In this case the use of the lines through the origin as an estimate of Klason lignin is an approximation only. This is also reflected in the magnitudes of the standard error of the estimates calculated from both lines. From Table XVIII it is seen that the standard errors are significantly higher for the estimates from the line through the origin.

It is further seen from Table XVIII that the factors converting Kappa number to Klason lignin are approximately the same for all softwoods and fairly close for aspen, thus to a certain extent confirming Berzin's assumption that Kappa numbers generally can be converted to % Klason lignin by multiplying them by the factor 0.13, although the factor obtained from these experiments is higher. The factors converting Nu numbers to Klason lignin (Table XIX) are also approximately the same for all softwoods. The factor for aspen, however, is significantly higher, thus indicating that there exists no general factor converting Nu numbers to Klason lignin.

Regression Relationship of Kappa Number on Nu Number

Table XX shows that the regression lines of Kappa on Nu number have positive intercepts. It can be shown statistically that these intercepts are only slightly significant, indicating that the straight line through the origin is not significantly different from the regression line. In this case, the use of the line through the origin, instead of the regression line, would introduce only a slight additional error in the estimates. This is also reflected in the standard errors of the estimates (Table XX) which are only slightly higher than those estimated from the regression line. This is further illustrated in Table XXI where are shown the Kappa numbers found and those estimated from both the regression line and the line through the origin for all softwood cooks. The overall regression line was used for the calculations.

These results show that at the conditions used in these experiments there is a linear relationship between Kappa and Nu numbers and that the regression line passes through the point of zero Kappa-zero Nu number. Further, the results show that the Kappa numbers may be estimated with an error of about $\pm$ 2.5% for softwoods and about $\pm$ 4% for aspen.

The softwood cooks were performed under identical conditions. The aspen cooks, however, were performed under varying conditions, as shown in Table X. The standard error of estimates indicates that the variables introduced in this manner have no significant influence on the relationship between the Kappa and Nu numbers for aspen. It is reasonable to assume that this would be true with respect to the softwoods also. This is in contrast to the marked influence that variations in cooking conditions and in wood species had on the correlation between lignin in pulp and lignin in liquor.

TABLE XXI

COMPARISON OF Kappa NUMBERS FOUND AND ESTIMATED FROM Nu NUMBERS

(Laboratory cooks)

Sample	Kappa Numbers		
	Found by Analysis	Estimated from Regression Line	Estimated from Line Through Origin
Loblolly pine	140	144	145
	128	126	126
	101	98	98
	146	148	149
	119	116	116
	93	92	92
	44.3	45.9	44.7
Mean values	110.1	110.0	110.1
Black spruce	151	145	146
	132	133	133
	106	106	106
	98.7	100	100
	80.1	84.4	84.0
	64.7	63.5	62.6
	66.2	66.5	65.7
Mean values	99.8	99.8	99.6
Southern pine	140	140	140
	135	134	134
	109	105	105
	101	95.4	95.2
	93.5	92.0	91.6
	62.4	63.0	62.1
	64.8	64.7	63.9
Mean values	100.8	99.2	98.8
Douglas-fir	135	141	142
	126	124	124
	109	104	104
	90.6	93.6	93.4
	81.9	84.4	84.0
	61.6	63.4	62.6
	61.7	60.4	59.5
Mean values	95.1	95.8	95.6

The conversion factor for Kappa number to Klason lignin was found to be approximately the same for both softwoods and aspen. This is not true, however, for the factor converting Nu numbers to Kappa numbers, indicating that this factor must be determined in each case in order to express the results in Kappa numbers.

The correlation coefficients show a very high correlation between the three parameters. The correlation is more quantitatively expressed by the coefficient of determination, which is defined as the square of the correlation coefficient. This quantity is used to determine the percentage variation in the dependent variable caused by errors in the independent variable. Applying this quantity to the results, it is found that in more than 98% of the cases a variance in the Kappa number is reflected in the Nu number.

Commercial Pulps

The Nu numbers of the commercial pulps are shown in Table XVII, and the corresponding values for Kappa number and Klason lignin are in Table XII. These data were treated statistically in the same manner as the data for the laboratory pulps. In Table XXII are given the regression relationships for Klason lignin on Kappa number, and in Table XXIII are similar data for Kappa number on Nu number. Figure 22 shows the mean regression line of Klason lignin on Kappa number for all of the commercial pulps, and Fig. 23 shows the same thing for Kappa number on Nu number.

Table XXIII shows that the intercepts of the regression lines of Kappa on Nu numbers vary from negative to positive values. The intercepts of the regression lines for Mills 1, 3, 4, and 7 are not significantly different from zero, while the other intercepts are definitely significant. However, the standard error of estimates from the lines through the origin have only slightly higher

TABLE XXII

REGRESSION RELATIONSHIPS OF Kappa NUMBER ON KLASON LIGNIN
FOR COMMERCIAL PULPS

Mill No.	No. of Tests	Regression Line	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %
1	17	% $\underline{KL}$ = 0.14 + 0.123 Kappa	0.894	0.140	3.9	% $\underline{KL}$ = 0.128 Kappa	0.140	3.9
2	14	% $\underline{KL}$ = -0.23 + 0.160 Kappa	0.961	0.270	2.9	% $\underline{KL}$ = 0.157 Kappa	0.280	3.0
3	11	% $\underline{KL}$ = -0.14 + 0.162 Kappa	0.988	0.085	1.7	% $\underline{KL}$ = 0.157 Kappa	0.850	1.7
4	12	% $\underline{KL}$ = -0.28 + 0.160 Kappa	0.986	0.110	2.5	% $\underline{KL}$ = 0.151 Kappa	0.130	2.8
5	12	% $\underline{KL}$ = 0.58 + 0.135 Kappa	0.994	0.105	1.4	% $\underline{KL}$ = 0.147 Kappa	0.115	1.6
6	12	% $\underline{KL}$ = -1.66 + 0.189 Kappa	0.978	0.115	1.9	% $\underline{KL}$ = 0.148 Kappa	0.150	2.5
7	12	% $\underline{KL}$ = -2.15 + 0.176 Kappa	0.833	0.790	5.0	% $\underline{KL}$ = 0.155 Kappa	0.880	5.6
All samples	90	% $\underline{KL}$ = -0.45 + 0.160 Kappa	0.998	0.270	3.5	% $\underline{KL}$ = 0.151 Kappa	0.300	4.0

TABLE XXIII

REGRESSION RELATIONSHIPS OF Kappa ON Nu NUMBER
FOR COMMERCIAL PULPS

Mill No.	No. of Tests	Regression Line	Correlation Coefficient	Standard Error of Estimate	Relative Error of Estimate, %	Line Through Origin	Standard Error of Estimate	Relative Error of Estimate, %
1	17	Kappa = -1.18 + 0.612 Nu	0.980	0.57	2.0	Kappa = 0.590 Nu	0.70	2.5
2	14	Kappa = -13.9 + 0.788 Nu	0.984	0.81	1.4	Kappa = 0.639 Nu	1.12	1.9
3	11	Kappa = -4.9 + 0.731 Nu	0.980	0.35	1.1	Kappa = 0.633 Nu	0.50	1.6
4	12	Kappa = -0.27 + 0.713 Nu	0.984	1.3	4.4	Kappa = 0.707 Nu	1.3	4.4
5	12	Kappa = -12.3 + 0.820 NU	0.964	1.3	2.6	Kappa = 0.658 Nu	1.55	3.1
6	12	Kappa = 11.67 + 0.408 Nu	0.962	0.55	1.4	Kappa = 0.572 Nu	0.98	2.4
7	12	Kappa = 0.6 + 0.631 Nu	0.976	1.4	1.4	Kappa = 0.635 Nu	1.4	1.4
All samples	90	Kappa = 0.2 + 0.630 Nu	0.921	1.9	3.9	Kappa = 0.631 Nu	1.9	3.9

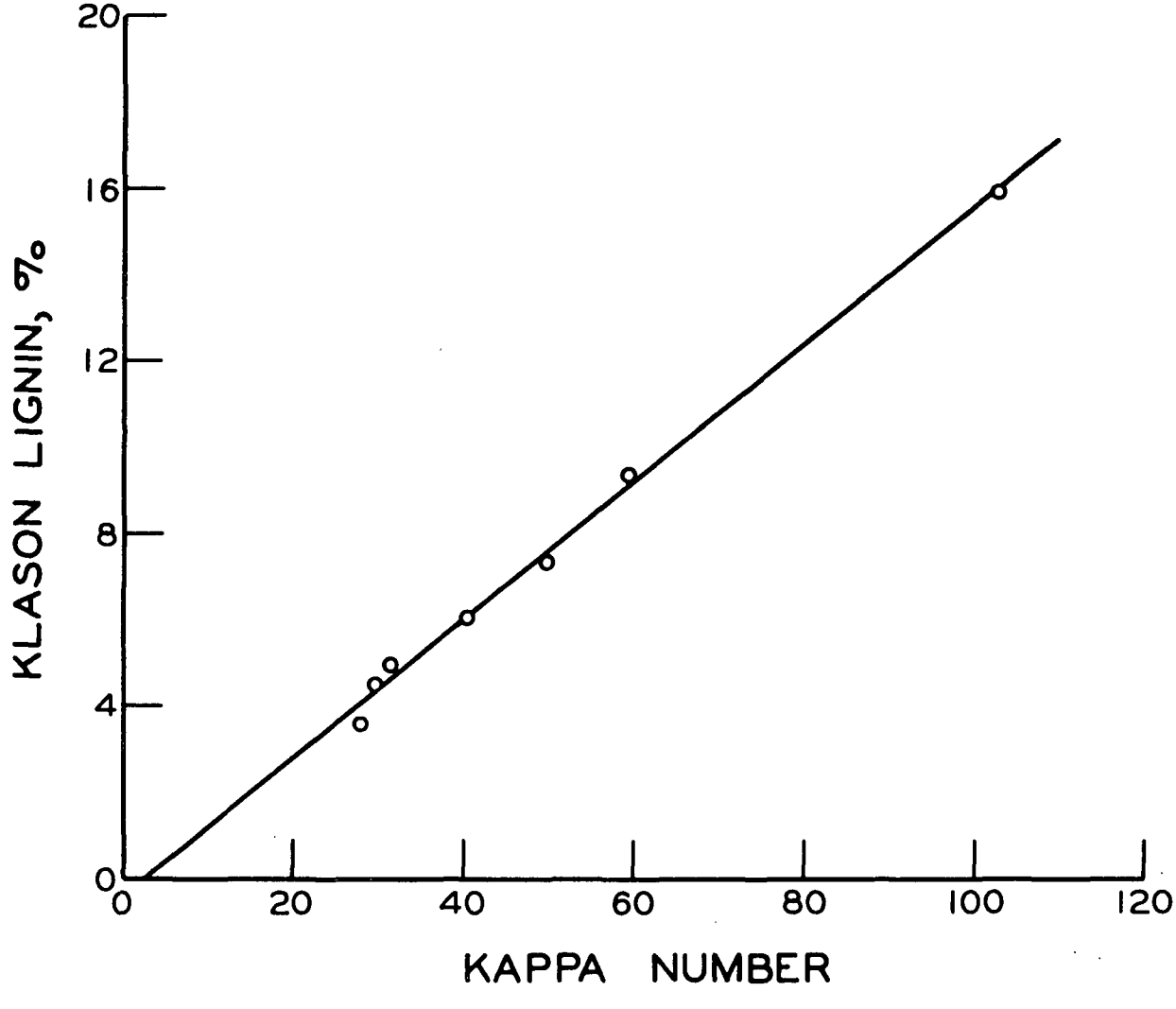

Figure 22. Mean Regression Relationship of Klason Lignin on Kappa Number for Commercial Pulps

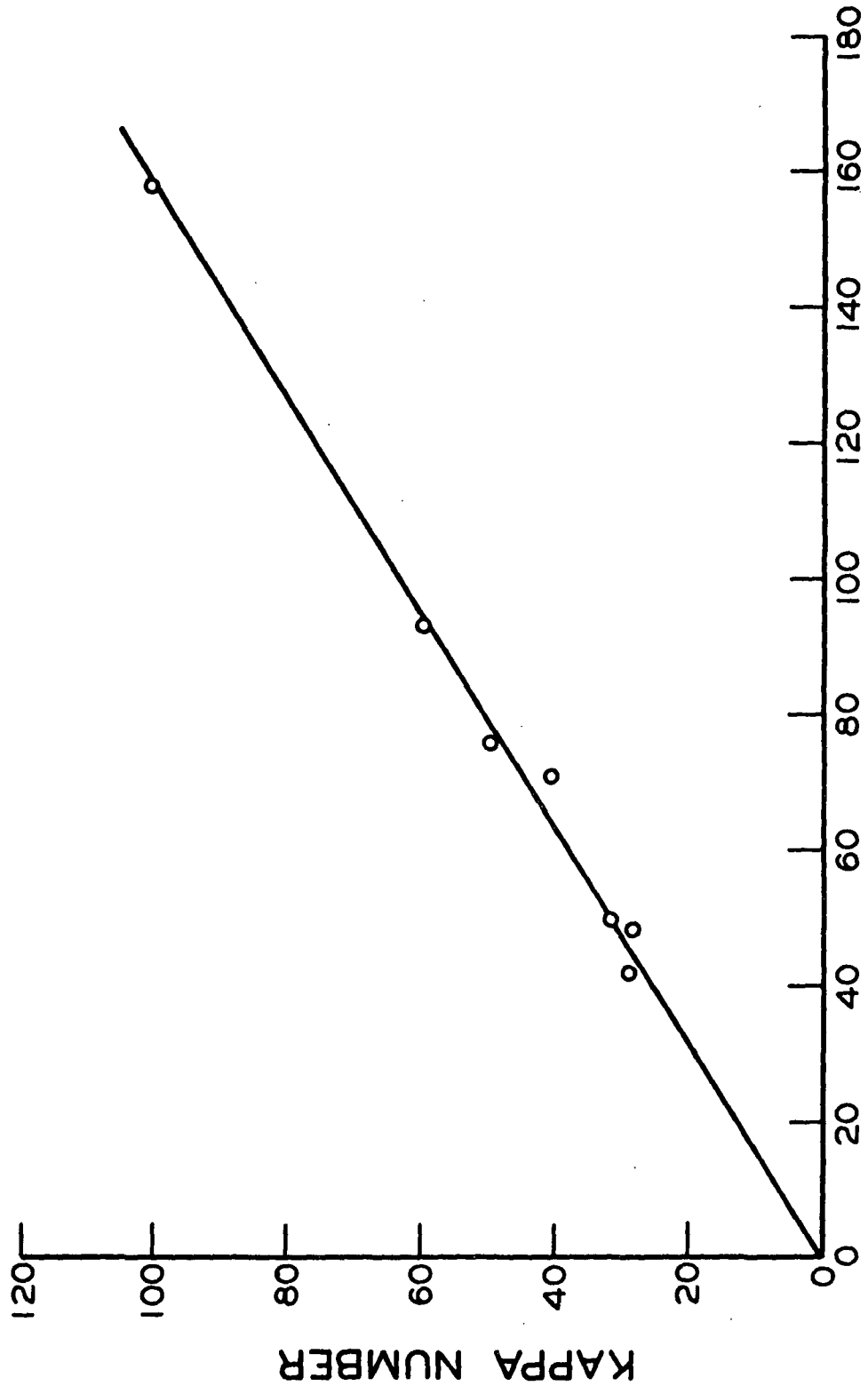

Figure 23. Mean Regression Relationship of Kappa Number on Nu Number for Commercial Pulps

values than those estimated from the regression lines, thus indicating that if the lines through the origin instead of the regression lines are used for obtaining estimated Kappa numbers from experimental Nu numbers, only a slight additional error is introduced. It is noted from Tables XII and XVII that the Kappa numbers and Nu numbers from each mill cover a very narrow range (max. 20 Kappa) compared with the ranges covered in the laboratory cooks (15-140). Consequently, any errors in the determination of the two parameters will influence the slope of the regression line to a greater extent for the mill samples than for the laboratory pulps.

However, when all the samples are considered together, the Kappa number range is considerably increased (18-110) and the regression relationship based on these data give a better estimate of the true relationship between the two parameters. In Table XXIII are shown the regression relationships calculated on this basis. It is seen that this line does not differ significantly from the line through the origin, indicating that the true regression line, shown in Fig. 23, passes through the origin.

The samples used in this study were chosen to represent different kinds of softwoods, digester types, and locations. Table XIII shows that, although the cooking conditions varied somewhat, as a whole, the samples may be considered fairly representative of pulp produced by the kraft process.

It can be seen that the development of the Nu number method has been based on its correlation with two other methods of lignin determination: the Kappa number method and the Klason lignin method. All three procedures were applied to the commercial pulps, and the analytical results are shown in Fig. 24. These three methods have their own limits of precision, as illustrated by the standard deviations shown in Table XXIV.

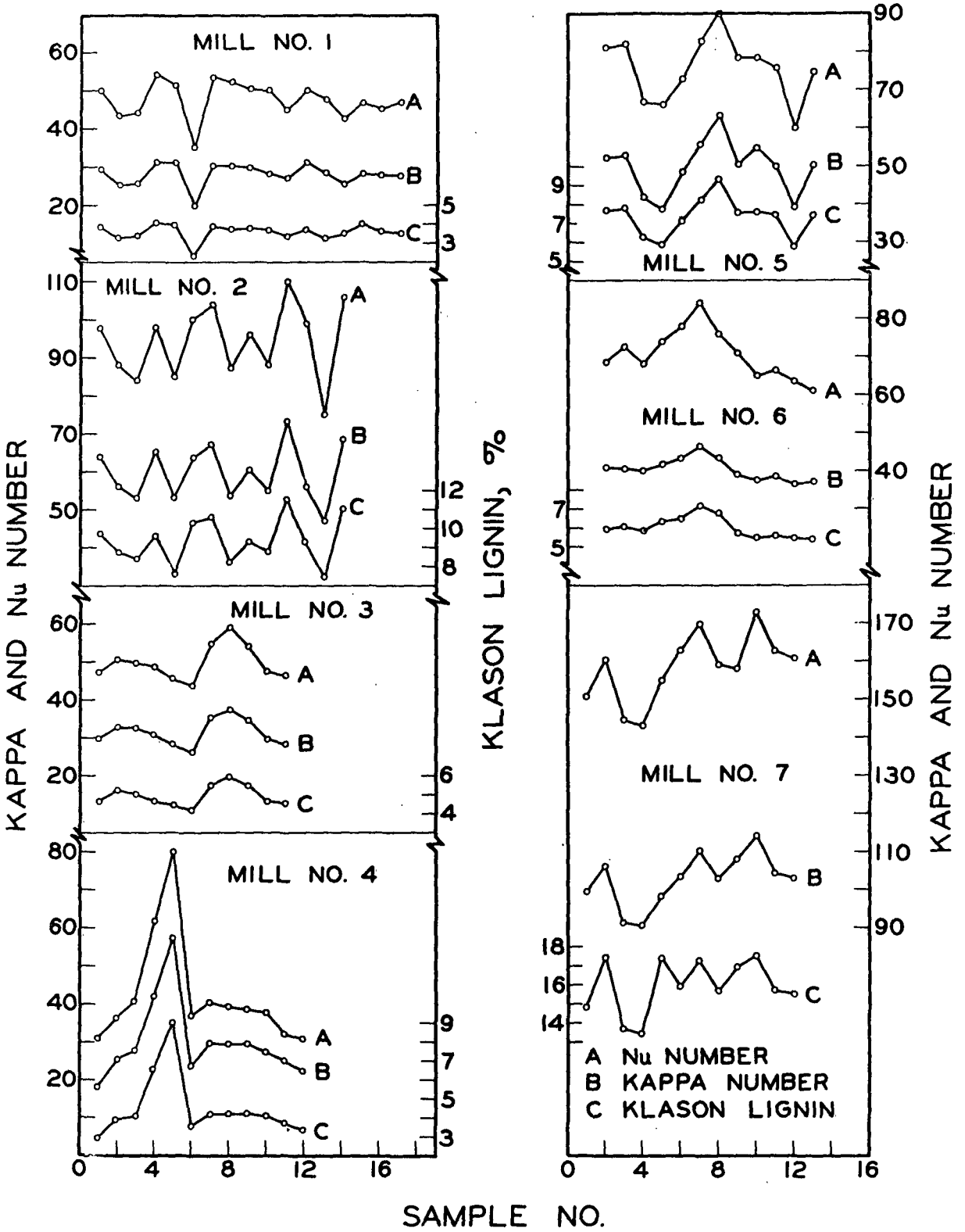

Figure 24. Results of Lignin Analyses for Commercial Pulps

TABLE XXIV

STANDARD DEVIATIONS FOR THE THREE METHODS
USED FOR MEASURING LIGNIN IN PULP

Test	No. of Tests	Mean Value	S	S Rel., %
Kappa no.	58	61.6	0.55	0.9
Nu no.	36	121	2.1	1.7
Klason lignin	55	10.7	0.35	3.3

CONCLUSIONS AND DISCUSSION

Despite promising results obtained in initial experiments with various methods of measuring lignin in liquor, the conclusive studies show quite definitely that present techniques do not yield results of acceptable precision. The regression lines given in Table XVI and shown in Fig. 19 are indicative of the strong influence of varying cooking conditions on the nature of the dissolved lignin. While the correlation between lignin in liquor and lignin in pulp is rather good, as shown by the high correlation coefficients in Table XVI, the relative error of estimating lignin pulp from lignin in liquor is as high as 22%, with an overall error of $\pm$ 12%. While the aspen cooks were made under varying conditions, the softwood cooks were not, and it can be seen from Table XVI that the relative error of estimating lignin in pulp from lignin in liquor for even these cooks is as high as 14%.

The attraction of measuring lignin in liquor as an inverse function of lignin in pulp resides in the relative ease of automatic liquid sampling and handling compared to automatic solid sampling and handling, particularly during the course of the digestion period. In view of this basic attraction, the conclusions required by the results of this study are perhaps disappointing. It can be seen, however, that in contrast to the closely controlled laboratory

cooks, industrial operations involve conditions, and a degree of variance of these conditions, that would only tend to widen the limits of error based on lignin in liquor measurements. Some of these conditions are: the reuse of black liquor, variance in liquor-to-wood ratio caused by a number of factors such as variations in wood charge, and wood moisture, relatively small variations in concentration of white liquor components, and variations in wood species, all of which apparently influence the nature of the lignin in solution.

The laboratory cooks made for this study were conducted in such a manner that a pulp yield range of 70% to 45% was covered, resulting in black liquors with a correspondingly wide range of lignin concentration. In any given pulp mill this range would, of course, be at least partly covered from the beginning of the cook to the end, but, assuming the method were to be used to control the end of the cook, only a very narrow range of lignin in liquor would be of prime interest. If the factors contributing to the error limits of the method were controlled reasonably well, it is quite possible that the lignin in liquor method could be used as a purely empirical tool, and that error limits, or measurement variance, could be reduced to acceptable dimensions. The results, of course, would be largely relative. It is of interest to note that the same laboratory cooks were used for the lignin in liquor studies and for the lignin in pulp studies, and, as can be seen from the data analysis, the lignin in pulp methods yield results of completely acceptable precision for process control.

Despite the long-standing tradition of using potassium permanganate as an oxidimetric reagent for measurement of lignin in pulp, the procedure used is empirical, and the results are defined by the conditions used for the test. Because of the universal use of the permanganate method, its direct automation

has a certain appeal. Not only the initial experiments in this direction, but also a detailed consideration of the requirements of the test conditions led to abandonment of further attempts at its automation. The consequent search for an equivalent method more amenable to automation led to the nitric acid, or Nu number, method.

The reaction of nitric acid with lignin in pulp is, as in all lignin chemistry, a difficult one to assess. However, some insight may be gained from an examination of the literature on the subject and from experiments performed during development of the method. The absorption maximum at about 425 nm., shown in Fig. 11, is evidently due to an intermediate product since it is shown by the reaction rate curves in Fig. 14, 15, 20, and 21, that it goes through a maximum intensity. Additional experiments have shown that this absorption maximum finally disappears upon prolonged heating. The peak at about 340 nm., however, increases in absorption intensity during prolonged reaction.

Bartunek obtained this peak upon reaction of phenol with nitric acid, an indication the product causing the peak is an aromatic nitro compound. There is some evidence that nitrous acid is a catalyst in this reaction. Sobolev (37) has shown that when 4-methyl guaiacol, a simplified lignin model with no side-chain oxygen, is treated with 16% aqueous nitric acid at 70°C., 4-methyl-nitroso-guaiacol is formed as a first intermediate. He suggested that the reaction proceeds by the special nitration mechanism described by Ingold and co-workers (38). According to this mechanism, initial attack on the aromatic nucleus is by nitrosium ion (NO^+) derived from molecular nitrous acid (which always is present in concentrated nitric acid):

$$HNO_2 + HNO_3 \rightleftarrows H_2NO_2^+ + NO_3^- \quad (9)$$

$$H_2NO_2^+ \rightleftarrows NO^+ + H_2O \quad (10)$$

$$NO^+ + NO_3^- \rightleftarrows N_2O_4 \quad (11)$$

$$ArH + NO^+ \rightarrow ArNO + H^+ \quad (12)$$

$$ArNO + HNO_3 \rightarrow ArNO_2 + HNO_2 \quad (13).$$

Sobolev was able to show that the reaction was inhibited by adding urea which destroys the nitrous acid. This inhibiting effect was confirmed in this work when, upon adding a small amount of urea to the nitric acid, the spectrum of the filtered reaction mixture failed to show a peak at 425 nm.

Since intermediate reaction products tend to be unstable, and the Nu number method is apparently based on the measurement of an intermediate, determination of the reaction rate curve for each pulp type seemed desirable during the development work. This insured that the color intensity measurements would be made under conditions of maximum stability. The temperature of 70°C. chosen for the development work permitted maximum color development in reasonably short times, yet resulted in a stability maximum with a plateau sufficiently broad to insure against premature decomposition before color intensity measurements were made.

In industrial application of the automated procedure, the heating time for maximum color development must be considerably shortened over that used in laboratory work. This can be accomplished, in effect, in two different ways. One way, of course, is to simply raise the reaction temperature, thereby increasing the reaction rate. Figure 25 shows that the time for maximum color development at 85°C. is only about ten minutes, although the plateau is relatively narrow. The other way to shorten the heating time is to make the color measurement

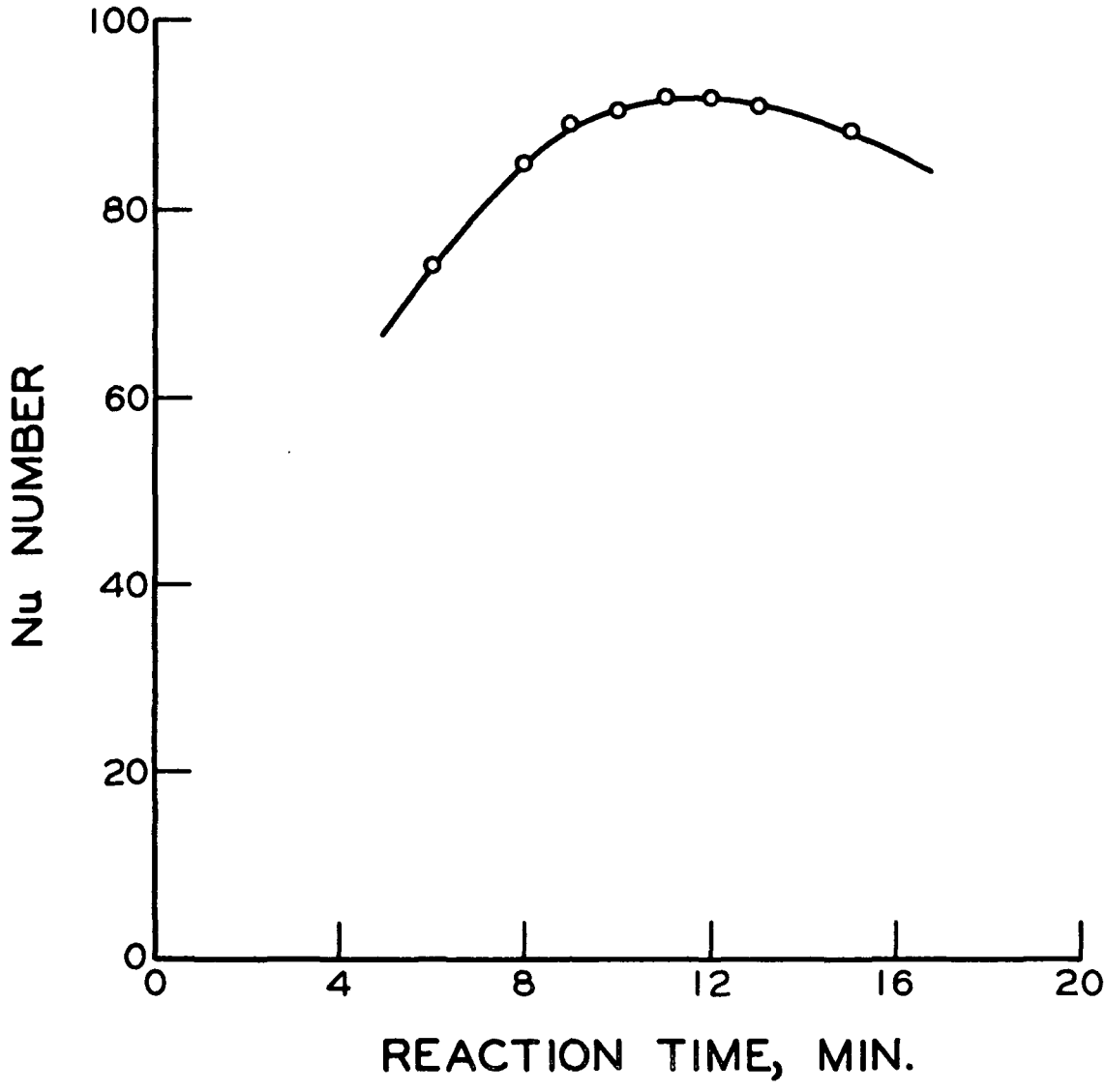

Figure 25. Reaction Rate Curve at 85° of Mill No. 2 Pulp with HNO_3

before the plateau in the reaction rate curve is reached. This can be successfully done in an automated system, because each sample can be processed in an identical manner, and the timing problems that would result in manual operation are eliminated.

Using the individual regression relationships shown in Table XXIII, Kappa numbers can be estimated from Nu numbers in individual cases with a precision of about $\pm$ 2%, with one exception. Using the mean regression line through the origin, illustrated in Fig. 23, the precision becomes $\pm$ 4%, using the mean conversion factor of 0.63. For the laboratory softwood pulps, the individual regression lines passed through the origin, as did the mean regression line. Here, the estimates of Kappa number from Nu numbers could be made from either relationship with equal precision ($\pm$ 2%), using a conversion factor of 0.44, despite the difference in wood species. Since the softwood laboratory cooks were made under the same conditions for all species, the conclusion seems to be that variance in softwood species cooked has no influence on the Nu number of the pulps produced. By a similar method of reasoning from the results of the aspen cooks, which were made under varying cooking conditions, it appears that realistic variations in digestion practice have no significance on the Nu number measurements.

That the individual regression lines of the commercial pulps did not all pass through the Kappa no.-Nu no. origin, in contrast to the laboratory pulps, with an attendant higher error in estimations of Kappa numbers from Nu numbers, must be attributable to differences in pulping practice other than variations in wood species or cooking conditions. One of these differences conceivably could be in commercial barking practice. The wood used for the laboratory cooks was completely free from bark, but it is doubtful if the same is true of any of the wood from which the commercial pulps were produced.

Another difference is the commercial practice of reusing black liquor which, when digested a second time, may leave a residue on the pulp that, while probably small in amount, may affect the reaction with nitric acid.

However, the major reason for failure of the individual regression lines to pass through the origin is, as explained on page 75 and 80, that the narrow range of values for each mill does not permit extrapolation of the regression line with a high degree of accuracy. Since the regression line of the mean values of all of the samples from all of the mills does intercept the point of zero Kappa-zero Nu, it can be said with some confidence that this relationship is actually valid for the individual mills also.

While the difference in precision of estimating Kappa numbers from Nu numbers is not great between the laboratory pulps and the commercial pulps, the conversion factor is considerably different. This difference is reflected in the spectrum of the filtered reaction mixture of the two types of pulps. For the laboratory pulps the ratio between the maximum absorption at 425 nm. and the minimum at about 400 is 1.6, while for the commercial pulps it is 1.3 under the previously defined conditions for measurement of the Nu number. The difference in this ratio seems to point to a difference in the nature of the lignin in the two types of pulp.

Despite these differences in precision and in conversion factors between laboratory-made pulps and commercially-produced pulps, the method of measuring residual lignin in pulp here called the "Nu number," has quite definite possibilities for adaptation to an automated procedure. Some of the features that make it attractive in this respect are:

1. No standard reagents are required.
2. Only one reagent is required.
3. The conditions of reaction can vary in a manner comparatively great without affecting the results significantly.
4. The method is widely applicable.
5. The results are directly related to the amount of lignin in the pulp, as illustrated in Fig. 24.

While these features make the Nu number method admirably suited for the purpose in mind, it shares a major problem with all pulp "hardness" tests in that they must be applied directly to the pulp. From this requirement arises the necessity of providing the automated procedure with a sample of pulp fibers automatically extracted from the process and automatically measured quantitatively. To do anything less would largely negate any automated features. Therefore, a compatible automatic sampling procedure must be devised.

FUTURE WORK

Continuing work on this development project will involve two different, but closely related phases: (1) further development of the Nu number method, and (2) development of a compatible automatic fiber sampling system. The two phases can, at this point, proceed simultaneously.

Most of the data in this report concerning the Nu number development were obtained by the procedure outlined on page 63. This procedure calls for the dry pulp to be ground so that it all passes through a 40-mesh screen. Obviously, this is an impractical requirement for an automated industrial system. A few brief experiments with several commercial pulps and several laboratory pulps indicate no essential difference in results or procedure between ground and unground fibers. However, additional work is needed to define the limits, if any, of the slurry consistency to which the method can be applied without excessive reagent consumption and distortion of the regression relationship between the Nu and Kappa numbers.

The procedure used so far also calls for a reaction mixture of 30 mg. of pulp in 50 ml. of 14% HNO_3. The consistency of this reaction mixture is, therefore, 0.06%, a requirement that, again on the basis of some few experiments, seems quite adjustable to more realistic proportions.

Both of these requirements of the procedure used so far, the use of ground pulp and the 0.06% consistency of the reaction mixture, are subject to change, but the consistency of the reaction mixture is dependent not only on the demands of the pulp-HNO_3 reaction, but also on the limitations of the sampling system to be devised. It is expected that work now planned in the

laboratory and in one of the mills of one of the sponsors will provide data upon which the design of the sampling system can be based.

Because the design of the sampling system is considerably dependent on the features of the analytical system, nearly all of the effort expended to date has been directed toward selection and development of a suitable analytical system. With this phase nearly completed, major attention can now be given to the sampling system design.

Presently, two approaches are being considered for automated quantitative sampling of fiber slurries. One approach is outlined in the Research Proposal upon which this project is based, and involves utilization of the compressibility function of fiber mats in a water-saturated system. The other approach is based on recent developments in consistency regulation at relatively low consistency values. Most likely, the latter approach will be investigated first, mainly because of the relative simplicity of evaluating its suitability.

The nitric acid method has so far been applied to kraft pulps only. Its applicability to sulfite pulps has not yet been evaluated. Preliminary experiments, however, indicate that this method also may be used for this kind of pulp, although some difference in reaction paths has been observed. It is the intention to study this approach more thoroughly during the next phase of the project work.

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APPENDIX

FORMULAS FOR PAIRED COMPARISON OF TWO SETS OF RESULTS

The mean difference between the two sets of results was calculated from:

$$\bar{d} = \frac{1}{n} \sum^{n} (x_1 - x_2) = \frac{1}{n} \sum^{n} d \qquad (14)$$

where n are number of pairs and x_1 and x_2 the values of each set.

The standard deviation of $\bar{d}$ was found from the formula:

$$S_{\bar{d}} = \sqrt{\frac{1}{n-1} \left(\sum^{n} d^2 - \frac{1}{n} \left(\sum^{n} d \right)^2 \right)} \qquad (15).$$

The t-value for the mean difference was calculated from the formula:

$$t = \frac{\bar{d}}{S_{\bar{d}}} \sqrt{n} \qquad (16).$$

FORMULAS USED FOR CORRELATION ANALYSIS

The regression line was estimated from the linear regression equation

$$Y = a_{YX} + b_{YX}X \qquad (17)$$

where X and Y are the independent and dependent variables, respectively, a is a constant, and b the coefficient of regression.

The coefficient of regression was calculated according to the formula:

$$b_{YX} = \frac{\Sigma X \cdot Y - n \cdot \bar{X} \cdot \bar{Y}}{\Sigma X^2 - n\bar{X}^2} \qquad (18).$$

The constant a was determined from the relation

$$a_{YX} = \bar{Y} - b_{YX}\bar{X} \qquad (19).$$

The coefficient of correlation was calculated from the formula

$$r_{XY} = \frac{\Sigma X \cdot Y - n\bar{X} \cdot \bar{Y}}{\sqrt{(\Sigma X^2 - n\bar{X}^2)(\Sigma Y^2 - n\bar{Y}^2)}} \qquad (20).$$

The correlation coefficient adjusted for the number of cases was calculated from the formula

$$\bar{r}^2_{XY} = 1 - (1 - r^2_{XY})\left(\frac{n - 1}{n - 2}\right) \qquad (21).$$

The standard error of estimate was found from

$$\bar{S}_{YX} = \sqrt{\frac{\Sigma Y^2 - n \cdot \bar{Y}^2}{n - 1}(1 - \bar{r}^2_{XY})} \qquad (22).$$

If $\underline{Y}$ is regarded as the independent variable, the regression coefficient $\underline{b}$ is defined by

$$b_{XY} = \frac{\Sigma X \cdot Y - n \cdot \bar{X} \cdot \bar{Y}}{\Sigma Y^2 - n \cdot Y} \qquad (23),$$

and $\underline{a}_{XY}$ by

$$a_{XY} = \bar{X} - b_{XY} \cdot \bar{Y} \qquad (24),$$

giving the regression line

$$X = a_{XY} - b_{XY} \cdot Y \qquad (25).$$

The standard error of the regression coefficient is calculated from the formula

$$\sigma_{b_{YX}} = \frac{\bar{S}_{YX}}{\sigma_X \sqrt{n}} \qquad (26).$$

The mean estimated value of $\underline{Y}$ is defined by the equation

$$\bar{Y}' = a_{YX} + b_{YX} \cdot \bar{X} \qquad (27),$$

and its standard error is

$$\sigma_{\bar{Y}'} = \frac{\bar{S}_{YX}}{\sqrt{n}} \qquad (28).$$

Since the estimated value $\underline{Y}'$ equals $\bar{\underline{Y}}' + \underline{b}(\underline{X} - \bar{\underline{X}})$, the standard error of the estimate for any value of $(\underline{X} - \bar{\underline{X}})$ will be composed of the sum of the standard errors of $\bar{\underline{Y}}'$ and of $\underline{b}(\underline{X} - \bar{\underline{X}})$. The standard error of $\underline{Y}'$ for any particular value of $(\underline{X} - \bar{\underline{X}})$ is therefore given by the equation

$$\sigma_{Y'} = \sqrt{\sigma^2_{\bar{Y}'} + [\sigma_{b_{YX}}(X - \bar{X})]^2} \qquad (29).$$

Using this equation, the standard error of $\underline{Y}'$ can be calculated for selected values of $\underline{X}$.

The 95% confidence limits of the estimate, $\underline{Y}'$, are given by

$$Y' \pm t \cdot \sigma_{Y'} \qquad (30)$$

where $\underline{t}$ is the value obtained from a $\underline{t}$-distribution table for $(\underline{n} - 2)$ degrees of freedom corresponding to a probability point of 0.025.

In order to use the regression equation for future individual predictions when $\underline{Y}$ and $\underline{X}$ is measured, the standard error of the single future estimate is

$$\sigma_{Y'-Y} = \sqrt{\sigma^2_{\bar{Y}'} + [\sigma_{b_{YX}}(X - \bar{X})]^2 + \bar{S}^2_{YX}} \qquad (31).$$

This equation can be used to estimate the range within which the true value of the estimated value of $\underline{Y}$ will probably lie.

The 95% confidence limits are calculated as described above.